TU Clausthal

Materialwissenschaft und Werkstofftechnik

Lei Xie

Doctor Dissertation

Study on relevant factors influencing the strength of weld line defect in micro injection molding process

Prof. Dr.-Ing. Gerhard Ziegmann

Kunstofftechnik

Institute of Polymer Materials and Plastics Engineering

Study on relevant factors influencing the strength of weld line defect in micro injection molding process

Dissertation

Zur Erlangung des Grades eines

Doktor-Ingenieurs

Vorgelegt von

Lei Xie

aus Shanxi, P.R.China

genehmigt von der

Fakultät für Natur- und Materialwissenschaften

Der Technischen Universität Clausthal

Tag der mündlichen Prüfung

02.07.2010

Acknowledgement

At the moment of this dissertation finishing in Institute of Polymer Materials and Plastics Engineering, Clausthal University of Technology, I would like express my speechless appreciate to all the colleagues, friends and my family who supported, encouraged and guided me through all the duration of my doctoral research and study.

Especially, I want to say thanks to Prof. Gerhard Ziegmann, as my doctoral supervisor, his priceless guidance, encouragement, and support throughout this work help me finally reach the goal. He not only plays the role as the advisor in academic aspect, he is also a kind and helpful friend and eldership in my daily life. I learned not only the scientific knowledge but also the spirit and philosophy to being an active, motivated, passionate, thoughtful and helpful person, which I will benefit of in rest of my life. I also want to give my thanks to Prof. Michael Gehde for being the reviewer and defense opponent of my dissertation. His constructive suggestion and careful correction are quite helpful for me to improve the dissertation finally to be able to be published. And the thanks also would like to extend to Prof. Lothar Wagner for severing as the chair of my defense commission.

I am also really appreciated for the invaluable helps and supports from all the scientific and technical coworkers in the institute. I am feeling so lucky that I have such a chance to be able to work together with those wonderful persons. Without their supporting, the dissertation cannot be finished so smoothly.

In addition, thanks would like to be given to Mr. Michael. Zellmann from Institute of Nonmetallic Materials for WXRD measurement; Mrs. Silke Lenk from Institute of Metallurgy for SEM test and Mr. Thomas Peter for SEM and Profile Scanner measurements as well as Ms. Dipl. Anne Finger and Dr. Joerg Adams from Institute of Physical Chemistry in AFM measurement.

Last but not least, I express my deep sincere gratitude to my parents for their always supports and encouragements. I give my greatest appreciation to my lovely wife Meijuan Wu for her unconditional scarifying, giving and loving for me. Also thanks to her for bringing me a pair of lovely angles. They are my most precious treasures all my life.

Thank god for helping me to get all these wonderful things!

Lei Xie

July 2010, Clausthal-Zellerfeld, Germany

Abstract

As a novel cost-efficient fabrication technology for micro system parts, micro injection molding process was developed from the late 80s of last century, which has been widely applied for micro parts mass manufacture in fields of optics, information storage, biomedical engineering, sensors, transducers and actuators.

However, as conventional injection molding process, there are many parts defects occurring in micro injection molding process as well, such as short-shot, material burying, air traps, inhomogeneous shrinkage and weld lines. Among those defects, some are hard to avoid during the process, like weld line, which is resulted from the encounter of two melts flow fronts due to multi-injection gates, uneven cavity thickness and insert obstacles. Weld lines always lead to reduced mechanical property and surface quality of injection molded parts, whose strength is associated with various processing factors, like processing parameters, materials system, and mold design and so on.

The presented research work represents influencing mechanism of various related factors on micro injection molded weld line's mechanical properties. According to the special features of micro injection molding process compared with normal injection molding process, the main related factors to weld line's properties were classified as 3 group, named as processing conditions, mold design and structure, external process.

Regarding factors in the processing conditions group, the effect of micro injection molding processing parameters and nano fillers on micro weld line strength was investigated. Based on the Taguchi experimental method, with the polypropylene, the optimized processing condition and significant order of 6 processing parameters (melt temperature, mold temperature, injection pressure, packing pressure, ejection temperature and injection speed) were achieved. A prediction formulation of the strength of the micro weld line was built up by multiple regression analysis based on Chebyshev orthogonal polynomial. In order to reveal how nano fillers affect properties of the weld line defect in micro injection molding, polypropylene (PP) was compounded respectively with carbon nano fibers (CNFs) and TiO_2 nano particles at various weight fractions (10, 20, 30 35 wt%) through co-screws internal mixing. The morphological, thermal and rheological properties of nano composites were characterized by wider angle X-ray diffraction (WXRD), different scanning calorimeter (DSC) and high pressure capillary rheometer. And under the constant injection molding processing condition, micro tensile samples with weld lines for each nano filled PP composite were formed. The tensile tests were served as the characterizing method for weld line mechanical properties. The results show that with filling nano fillers, the weld line strength was decreased obviously, and due to the different geometry, the CNFs and TiO_2 have different influencing mechanism on micro weld line mechanical properties.

As for factors related to mold design and structure, the further understanding of polymer melts flowing behavior in micro scale cavity related to micro channel cross section shapes and injection gate dimensions has been implemented, which finally affects the mechanical properties of micro injection molded weld lines. The investigating results on influencing mechanism of cross section shapes on micro weld line strength show that there is one factor relating to cross section shape defined as the ratio of cross section perimeter to its area, the cross section shape with higher value of this factor corresponding higher micro weld line strength. For the effect of injection gate dimensions on micro weld line strength, the experimental strategy involves typical edge gates with various depth and width dimensions, in order to find out the response of micro weld line strength to those different gate sizes, whose results evidence the edge gate with small size leads to higher micro weld line strength which is unlike normal injection molding, and the depth dimension of the edge gate supply more contributions in affecting weld line strength than its width dimension.

Considering external process related factors, effects of the ultrasonic oscillation and the physical vapor deposit (PVD) metallic thin film on micro injection molded weld line properties were discussed. The achieved experimental results show that the ultrasonic assistant and the PVD thin film are proven to obviously improve the weld line strength in micro injection molding. Their inside working mechanism on enhancing weld line strength is analyzed as well.

Finally, a novel effective visualizing experimental method for observing polymer melts filling behavior in micro cavity is purposed and realized, which offers an approach to directly investigate weld lines forming and developing process during micro injection molding process. The hereby device and method allows the verification of validity of the simulation about micro injection molding process.

Keywords: Micro injection molding, Weld line, Nano composites, Design of experiment, Cross section shape, Injection gate dimension, Ultrasonic oscillation, Physical vapor deposit, Visualizing mold

Contents

List of Symbols

ΔH	Enthalpy of transition	[J]
K	Calorimetric constant	
A	Area under the differential scanning calorimetry measuring curve	[m^2]
T_g	Glass transition temperature	[C°]
T_m	Melting temperature	[C°]
T_c	Crystallization temperature	[C°]
R_m	Tensile strength	[MPa]
F_B	Maximum tensile force	[N]
A_o	Area of the initial cross-section	[m^2]
d_{hkl}	Distance of crystal lattice	
n	Diffraction level	
λ	Wavelength of the irradiation X-ray source	[nm]
θ	Bragg angle	[°]
L_{hkl}	Crystallite size	[nm]
k	Shape factor associated with the crystallites	
β_{hkl}	Half height of the feature peek	[Rad]
S/N	Signal-to-noise ratio	
y_i	Aiming experimental result	
n	Experimental times	
$F_{weld\ line}$	Predicted micro weld line strength by processing parameters	[MPa]
T_{melt}	Melt processing temperature	[C°]
T_{tool}	Mold temperature	[C°]
T_{demold}	Demolding temperature	[C°]

$V_{injection}$	Injection speed	[cm^3/s]
δ_w	Predicted micro weld line strength by nano filler contents	[MPa]
φ	Nano fillers concentration	
a_1	Constant efficient related to nanofiller features	
a_2	Constant efficient related to nanofiller features	
a_3	Constant efficient related to nanofiller features	
δ_m	Tensile strength of polymer matrix	[MPa]
a	Ratio of the micro channel cross section perimeter to its area	[1/m]
L	Perimeter of the micro channel cross section	[m]
S	Area of the micro channel cross section	[m^2]

List of Abbreviations

IC	Integrated circuit industry
MEMS	Micro electro mechanical systems
MS	Microsystem
MOEMS	Micro optical electron mechanical system
Bio-MEMS	Bio- Micro electro mechanical system
IT	Information technology
UV	Ultraviolet
3D	3 Dimensional
LIGA	Lithographie and galvanic
IB-LIGA	Ionic beam LIGA
EB-LIGA	Electronic beam LIGA
EDM	Electrical discharge machining
RTV	Room temperature vulcanization
PP	Polypropylene
HDPE	High density polyethylene
PS	Polystyrene
PBT	Polybutylenterephthalat
CNFs	Carbon nano fibers
DSC	Differential scanning calorimetry
TGA	Thermogravimetric analysis

SEM	Scanning electronic microscope
AFM	Atomic force microscope
WXRD	Wide angle X-ray diffraction
PLM	Polarized light microscope
ANOVA	Analysis of variance
wt%	Weight percent
CVD	Chemical vapor deposition
PVD	Physical vapor deposition
QMB	Quartz micro balance
Al	Aluminum
Ti	Titanium

Overview

1 Introduction

1.1 Motivation

Concepts for micro devices fabrication are started about 40 years ago because of the rising and developing of integrated circuit industry (IC) [1-2]. It has been widely used to construct various kinds of micro parts and components which start a first application in watch and camera industry, then extended to printer ink jet, information storage, sensors and transducers, micro fluidic system, micro heat exchanger, micro reactor etc. This field is well developed and becomes a new area named as micro electron mechanical system(MEMS) or microsystem(MS). Especially Micro optical electron system (MOEMS) and Bio- micro electron mechanical system (Bio-MEMS) occupied important positions in it, in the last 10 years, since the Information Technology (IT) and Bio-technology (Bio-T) played the significant role associating with the human's daily life and scientific technology development. Typical MOEMS application is involved in micro lenses/ lens array, micro mirrors, micro diffraction grating, optical sensors and spectrometers, micro optical waveguide, micro light splitter etc. Usual BioMEMS mainly are focusing on Lab-on-Chip parts, drug delivery systems, micro bio analyzer and reactors etc. Based on the recent study, an increase of the market in this field is from $12 billion in 2005 to $24 billion in 2009, due to the development in the market for rewritable (RW) heads, inkjet heads and micro displays [3-6].

A lot of micro system parts are constructed on the photonic materials (e.g. silicon, SU-8), since many experiences gathering from the integrated circuit industry (IC). However, most manufacturing technologies are time and cost consuming, as well as application restricted by

the limitation of materials properties (e.g. Lithography, dry and wet etching, vapor disposition etc.). Therefore, the more promising micro fabrication technology aiming to realize large scale production and high cost efficiency has to be developed and promoted.

The micro processing technologies of polymer materials are booming in the last 2 decades because of this initial drive, e.g. micro injection molding, hot embossing, roll imprinting etc. Polymeric materials are a wide range material class which offer unique thermal, mechanical, physical and chemical characteristics, so that they can satisfy and cover most requirements for main applications of micro systems. Mainly part of the polymer materials used in micro system parts fabrication is summarized in Table1-1[7].

Table 1-1 Polymers generally used in micro injection molding[7]

Acronym	Full name	Temperature stability (°C)	Properties	Structure
COC	Cyclo-olefine copolymer	140	High transparency	Amorphous
PMMA	Polymethylmethacrylate	80	High transparency	Amorphous
PC	Polycarbonate	130	High transparency	Amorphous
PS	Polystyrene	80	Transparent	Amorphous
POM	Polyoxymethylene	90	Low friction	Semi crystalline
PEA	Perfluoralkoxy copolymer	260	High chemical resistivity	Semi crystalline
PVC	Polyvinlchloride	60	Cheap	Amorphous
PP	Polypropylene	110	Mechanical properties	Semi crystalline
PET	Polyethylene terephtalate	110	Transparent, low friction	Amorphous/Semi Crystalline
PEEK	Polyetheretherketone	250	High temperature resistivity	Semi crystalline
PA	Polyamide	80-120	Good mechanical properties	Semi crystalline
PSU	Polysulfene	150	Chemical and temperature resistivity	Amorphous
PVDF	Polyvinylidenefluoride	150	Chemically inert, piezo-electric	Semi crystalline

Most of these polymer materials can be processed by injection molding process in principle. With new functions and steps integration and modification of this well-established process technology, a novel evolution of this process, namely micro injection molding, is set up and spread rapidly and widely in micro system parts fabrication, because of the following advantages:

-Processing time is short, suitable for large scale production
-Net shape molding, further process step is not required
-Can produce complicated 3D shape parts
-Easily realized by various industry companies, special equipments needless (like UV light source)

Micro injection molding is a new advanced technology which can realize the manufacture of fine and precision parts with micro-nano structures in lower cost and higher efficiency. This

novel advanced manufacturing technology started in the late eighties and has drawn more and more attention presently and will become a hot research topic in many specifics all over the world, which is the interdisciplinary of mathematical, mechanical, physical, materials and fluid dynamics [8-11].

Due to the higher precision and quality requirements of micro parts than standard size nowadays, the development theory of the molding problems, like poor strength weld line, voids, burning and not uniform shrinkage etc, are definitely needed to be understood completely.

The weakness of mechanical properties and surface appearance defects due to weld line, are unfavorable in injection molding parts, especially in micro injection molding process. Weld lines are formed during mold filling whenever two separated melt streams recombine. This occurrence is caused by the injection through multiple gates or as a consequence of flow around an obstacle. Since weld lines often result in reduced mechanical strengths and poor optical surface appearance of injection molded parts, there have been a great number of investigations about the effect of processing conditions on the weld lines.

However, as for research works about weld line mainly focus on the macro scale parts, only limited literatures concern with the micro scale weld line [12-13]. Like the normal injection molding process, the weld line properties are affected by many factors, which are related to processing parameters (temperature, pressure and shear rate etc.), material structure (filled/unfilled polymers), mold structures (gate, cavity and runner geometry etc.) and external assistant process (ultrasonic oscillation etc.). Nevertheless, due to the special processing features of micro injection molding process (micro scale parts dimension, high pressure/shear rate, high mold temperature, fast cooling speed), the resulting correlation between those influencing factors and weld lines properties will be different comparing with that of normal injection molding.

Therefore, there are still some open problems and themes related to processing conditions, mold design and construction, external processing conditions, regarding to the weld line issue in micro injection molding. All these problems desiring to be solved and investigated compose an intensive drive for the researching motivation about the weld live development in micro injection molding.

1.2 General Strategy

Based on the extended basic motivation mentioned above, the presented thesis supposes to carry out the systematical investigation on the defect of weld line in micro injection molding process. The philosophical research strategy of this thesis is schematically illustrated in Fig. 1-1.

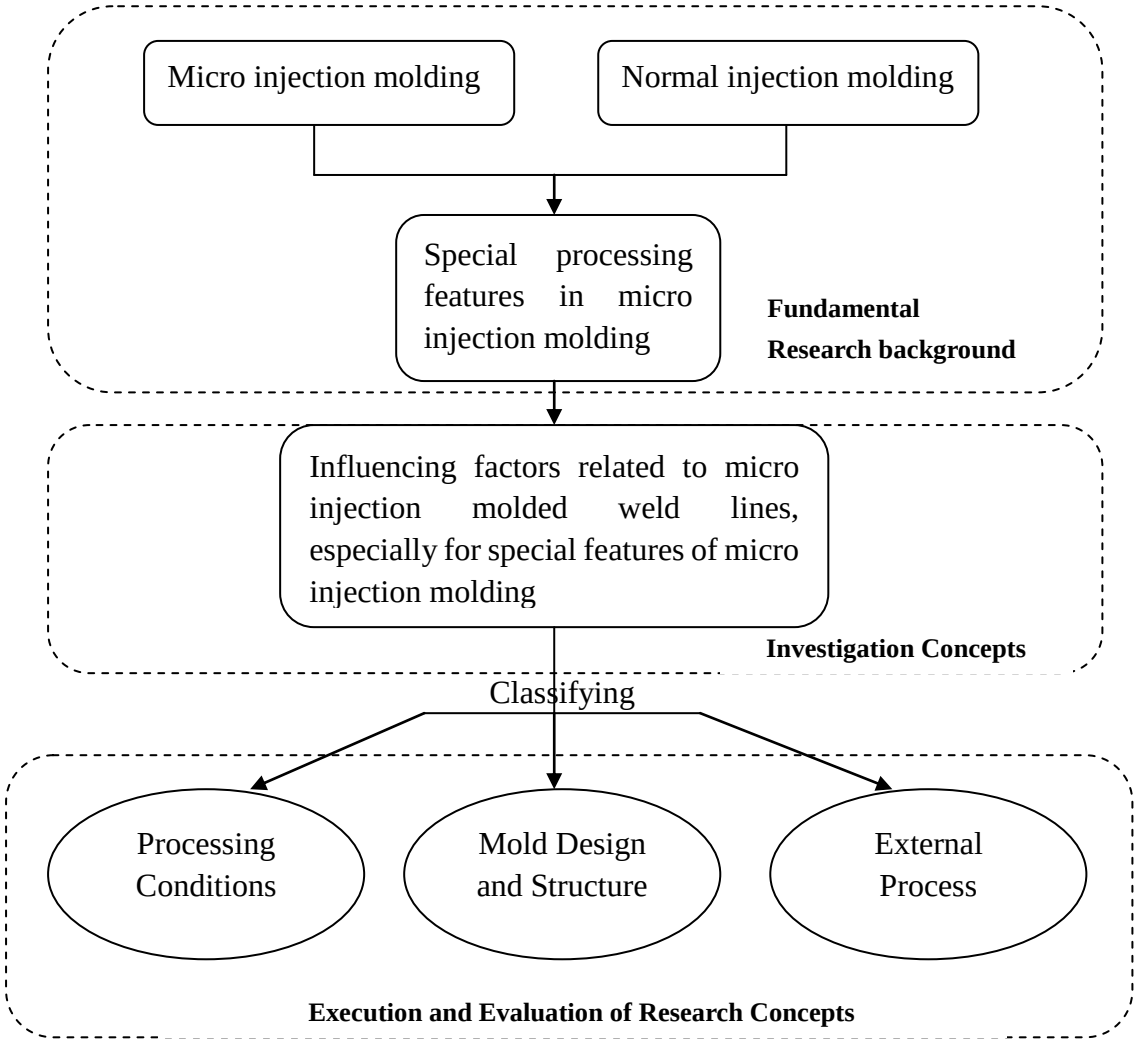


Fig.1-1 Schematic diagram of the philosophical investigation strategy of the presented thesis

The thesis will start from the base line of comprehensive understanding of micro injection molding process comparing with normal injection molding process, thus the special processing requirements in micro injection molding process are able to be found out and well defined. Based on this study of fundamental research background, the important and essential factors influencing strength of micro injection molding weld lines can be systematical listed and set up for constructing the investigation concepts which will guide the next further actual

scientific researching works, the main part of this thesis. Through the investigation on these 3 classified aspects, named as processing conditions, mold design & structure and external process, the rule of main factors influencing micro injection molded weld line will be figured out. It is worth mentioning that the results related to micro weld line strength finally gained in this thesis should supply some basic guideline and suggestion not only in scientific research but in real industry production for improving the micro plastic parts mechanical with weld lines defects.

2 Research background and State of the art

2.1 Micro injection molding

2.1.1 General Introduction

Satisfying the requirement of sharply increasing market for micro parts, the development of micro injection molding started in the late eighties, but no appropriate machine technology was available. Therefore, the well-known macroscopic injection molding, basic process cycle shown as Fig.2-1, is adapted to the micro scale by employing some special process steps [14-16].

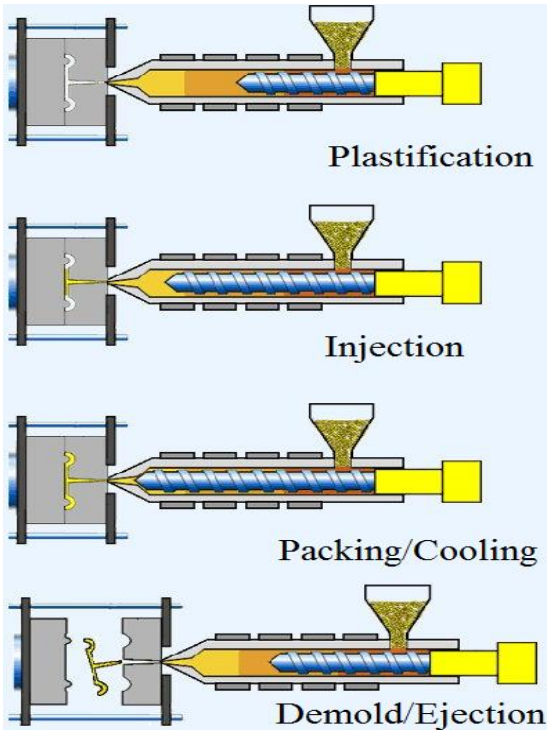


Fig.2-1 Normal injection molding process cycle (Source: Veltkamp)

Recently, as the development of micro tooling technology and research works of relative technique and basic investigation have been done in last 15 years [17-20], micro injection molding technology is improved dramatically and so far it is the most cost effective technology for manufacturing fine and precision parts with micro-nano structures. It allows producing singular micro parts or micro structured components from plastics, ceramics and metals. Micro Components are distinguished in micro system engineering as the following [21-22]:

A. Micro structured component with overall dimensions in millimeter or centimeter (macroscopic) range, but functional structures in magnitude of micrometers; (Fig.2-2a and Fig.2-2b);
B. Micro component with dimensions in micro meter range and masses of several mg; (Fig.2-2c and Fig.2-2d)
C. Micro precision component in conventional magnitudes, but with tolerances in the range of few micrometers; (Fig.2-2a)

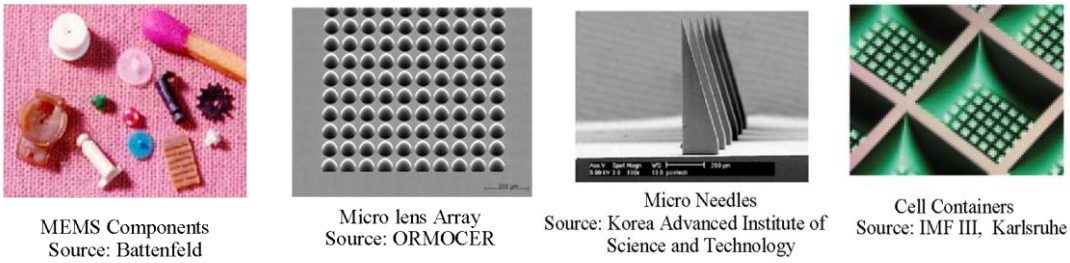


Fig. 2-2 Micro injection molding parts[23-26]

However, micro injection molding process is not just a scaling down of the conventional injection process. It requires a rethinking of each step of the process. Today, the micro injection molding generally comprises the following processing steps shown as Fig.2-3. Micro Injection Molding has special requirements for the injection pressure, mold temperature, vacuum of cavity, shot size and cooling speed, which are remarked as red fonts in the figure and could show different influences on weld line properties comparing with normal injection molding process.

The polymer melts fill into micro scale cavity through small sized runners and gates with high speed and high pressure, which can induce its degradation, but will help shear-thin effects [27]. The fabrication of high aspect ratio micro features can be realized by using a mold temperature close to the softening temperature of polymer or even higher [28–32]. In this way, some special structure sizes in the nanometer range also are able to be replicated [33].

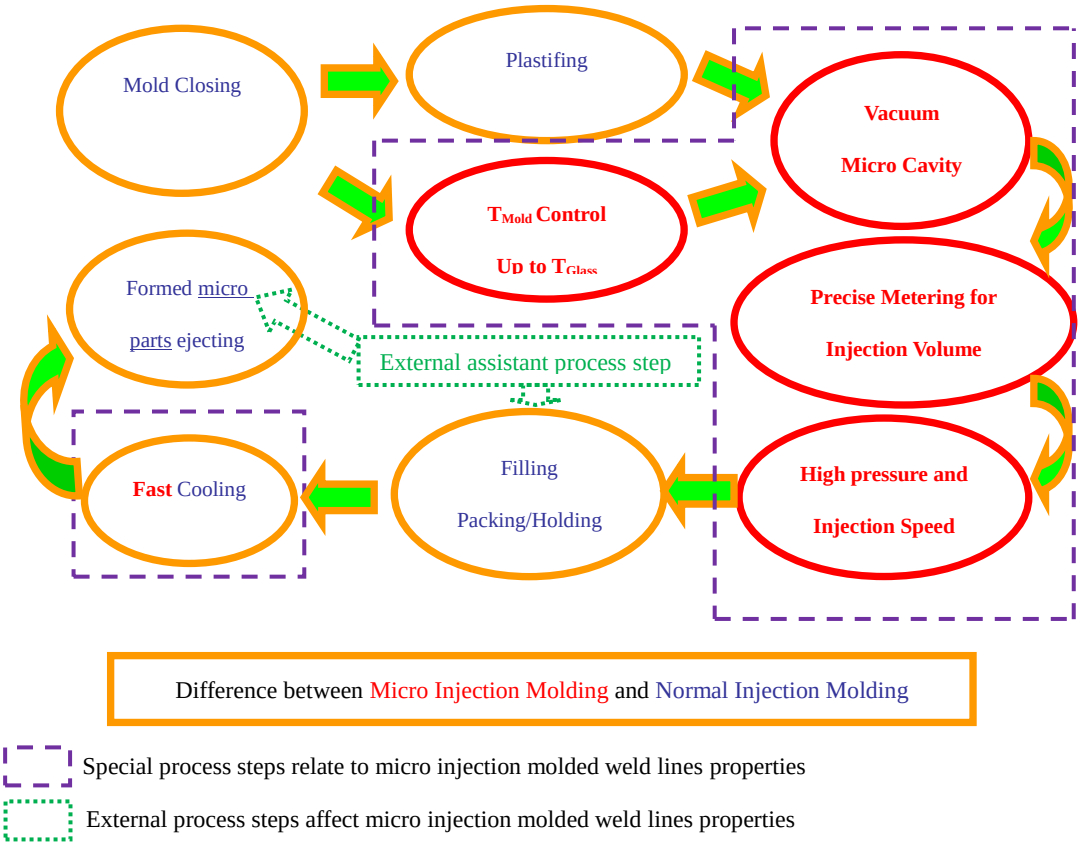


Fig. 2-3 Micro injection molding process steps

2.1.2 Micro Injection Molding Machine

During the early stage of micro injection molding, modified conventional machines, possessing clamp forces situated between 250 and 500 KN [34-35]. Because these machines' precision of shot-size is much larger than the micro parts' volume, the production of microparts with these machines is normally realized by multi cavities mould with large volume runner systems. It results in high amount of waste because the weight of the part represents only a few percent of the whole molded mass. A degradation can occur during the different processing steps (plasticization, injection, holding). Moreover, hydraulic control of the shot-size is not accurate enough for the replication of such small parts; thus electrical machines would be preferred for such application. In order to reach the new requirements for precise dosing, high speed/pressure and small clamping force in micro injection molding process, special micro injection molding machine is needed to develop and apply [36].

Table 2-1 List of commercial micro injection molding machine and their specifics

Name	Clamping force (KN)	Injection capacity (cm^3)	Injection Pressure (MPa)	Max. injection speed	Screw/plunger diameter(mm)
Arburg220s	150	15	250	112 cm^3/s	15screw
Dr. Boy 12M	129	4.5	245	-	12screw
Babyplast6/10	62.5	4	265	-	10 plunger
Battenfeld microsystem50	56	1.1	250	760 mm/s	14screw
APM SM-5EJ	50	1	350	800 mm/s	14screw
Lawton Sesame Nanomolder	13.6	0.082	245	1200mm/s	10plunger
Nissei AU3	30	3.1	-	-	14screw
Sodick TR05EH	49	4.5	200	300mm/s	14screw
Rondol High Force 5	50	4.5	160	-	20screw
Toshiba EC5-01 A	69	6	200	150mm/s	14screw
Fanuc Roboshots2000-1 5A	50	6	200	300mm/s	14screw
Summimoto SE7M	69	6.2	200	300mm/s	14screw
MCP12/90HSE	90	10	230	180mm/s	16screw

Currently, there are numerous of micro injection molding machines available in the commercial market, which could be classified into two main structures for micro injection molding machine:

1. Injection molding machine with the same principle as the conventional injection molding machine, but reduced screw diameter (under 20 mm), which can give a better metering precision of short size for micro parts, like Arburg® 220s. ;

2. Plastification unit and injection unit are separated, in which the plastifying unit consists of a smaller dimension screw to achieve precise dosing and homogenous plastifying, and injection unit constructed by a plunge to obtain high speed/pressure, like Battenfeld® Microsystem50 in Fig.2-4. The main available commercial micro injection molding machines are listed in Table 2-1. Nevertheless, some new technologies, such as ultrasonic, micro temperature and pressure sensors, are continuing to be applied to make the micro injection molding machine perfect in plastifying unit, control unit and process monitoring unit [37-38].

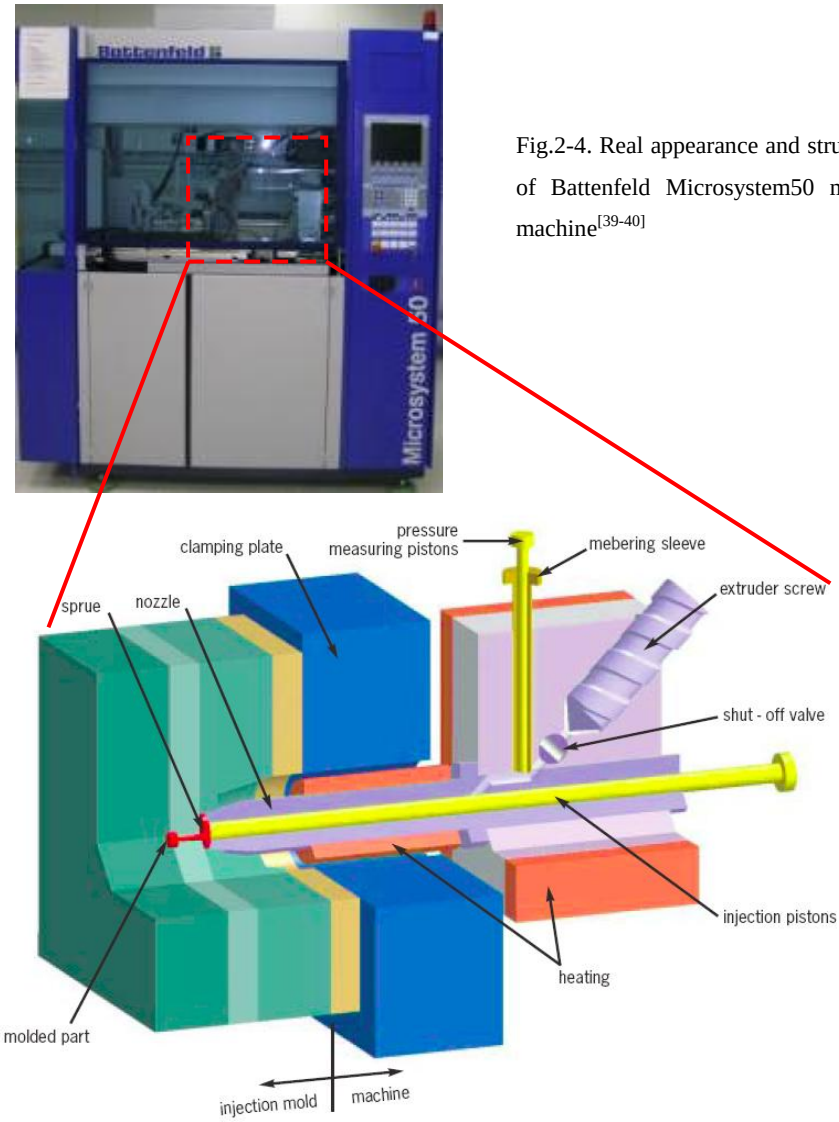


Fig.2-4. Real appearance and structure schematic drawing of Battenfeld Microsystem50 micro injection molding machine[39-40]

2.1.3 Fabrication technology for micro scale cavity inserts of injection mould

Mold inserts used in micro injection molding process are required to produce microstructured plastic parts, and in some cases to have special surface quality and functions. Their micro scale dimensions and high precision requirements demand specific methods for the mold inserts fabrication, summarized in Table2-2.

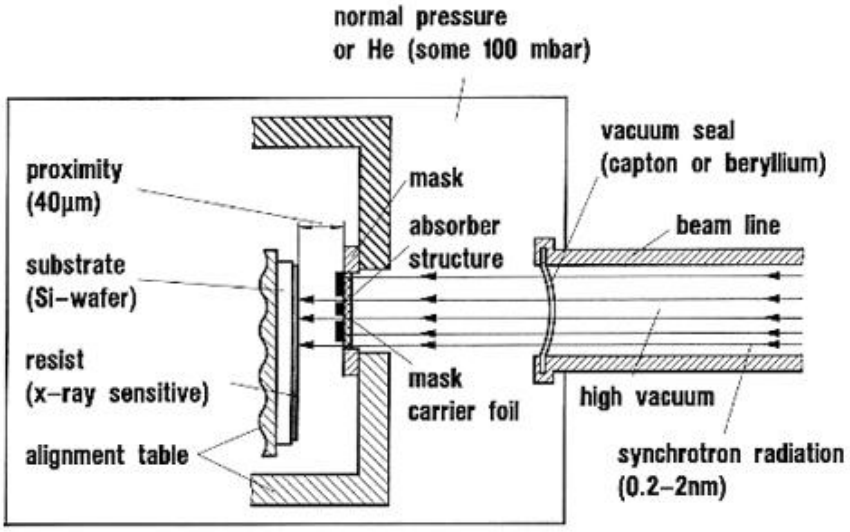
Table2-2 Special requirements for typical microstructured parts in various applications

Micro parts	Application areas	Technical Requirements
Micro lens	MOEMs	Surface roughness < 20nm
Micro fluidic system	Biomedical, Genetic analysis	Bio/ Chemical compatible, precise channel profile, super magnesium
Bipolar plate with micro structure	Fuel Cell	High thermal stability, conductivity
Optic Fiber Connect Ferrule	Tele communication	Concentricity < 0.0005mm

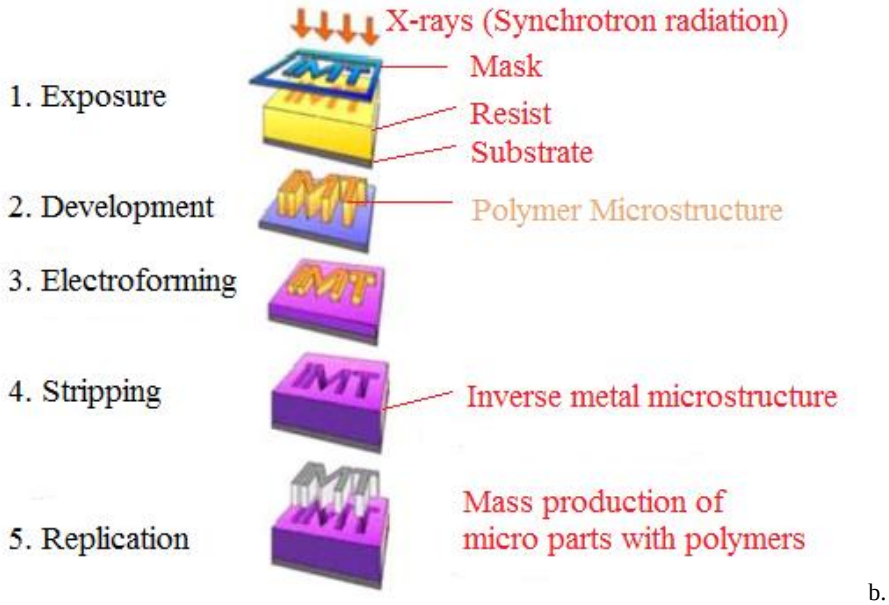
The main usual technologies are listed in the following:

- LIGA

The name of this process is abbreviation of the German words, Lithographie and galvanic, which means lithography and electroplating in English. Depending on the light resource applied during LIGA, it is branched as several extended processes, namely X-ray-LIGA, UV-LIGA, IB-LIGA and EB-LIGA[41-44]. Among them, X-ray-LIGA is available in higher aspect-ratio and precision micro structure preparation (schematic equipment and procedures are shown in Fig.2-5[45]). However, it is difficult to build the 3D geometry with undercut structures.



a.



b.

Fig.2-5 a. The schematic structure of X-ray Lithography equipment; b. The typical LIGA process procedures

- Micro machining process

In this group, micro milling and single point diamond turning are the usual options selected by the micro injection mould maker. Micro milling can profile complicate 3D micro structures, but the mould materials are limited to the soft metal, like copper and aluminum, additionally when the dimension is lower than 25 micrometer, the micro milling will hardly reach it and the surface quality of the machining surface is relative rough [46-48]. Single point diamond turning can supply perfect surface quality of the mould and suitable for some 3D structures machining, however it is also restricted in complex 3D geometry building [49-51].

- Electrical Machining

Micro electrical discharge machining (Micro EDM) is also one good assistant micro molding technology which is usually combined with the other molding processes [52-53].

-Etching

Various wet etching, dry etching processes are most popular micro fabrication methods in semiconducting materials, especially in materials based on silicon. They also can be used to prepare the micro injection molding mould insert, since the silicon wafer is also able to be applied as the mould material in injection molding process. Nevertheless, it is mostly implemented in labor scale mould, because of the short life time of silicon wafers [54-58].

Table 2-3 Comparison of various micro structuring molds inserts fabrication processes

Technology/feature geometry	Typical structure size	Feature tolerance	Aspect ratio	Wall roughness	Materials
Ion beam LIGA/2D	0.1 to 0.5 μm	0.02 to 0.5 μm	1	n/a	
Focused ion beam/2D & 3D	0.2 μm	0.02 μm	n/a	n/a	Any
X-Ray LIGA/2D	0.5 μm to 1 mm	0.02 to 0.5 μm	10–100	<20 nm	Electroformable Materials: copper, nickel and nickel alloy
Electron beam LIGA	0.1–0.5 μm		1–2	n/a	"
UV-LIGA/2D	2–500 μm		1–10	n/a	"
Femto-second laser 2D/3D	1 μm	<1 μm	1–10		Any
Excimer laser 2D/3D	6 μm	<1 μm	1–10	1 μm–100 nm	Polymer, ceramics and metal to a lesser degree
Ultra short pulses ECM 2D/3D	Few micrometers	<1 μm	8		
μEDM 2D/3D	10–25 μm	3 μm	10–100	0.3–1 μm	Conductive materials
Micromilling/2D or 3D	25 μm	2 μm	10–50	Few microns	PMMA, aluminum, Brass, steel
Deep UV resists	n/a	2–3 μm	22	≈1 μm	n/a
Deep reactive ion etching	n/a	<1 μm	10–25	2 μm	Silicon

There are also a lot of the other methods for micro molding, like laser machining, rapid protyping and orientation deposition etc. [59-63]. In the micro injection molding mould preparation, generally it is a combination process for various micro molding methods, like the LIGA technique and μEDM combination are widely used for the realization of mold inserts, because of the high aspect ratio and the tight dimensional tolerances obtained[64].

A comparison of the mold insert manufacturing techniques is proposed in Table 2-3, sorted as a function of the reachable structures sizes [17,18,65-68].

2.1.4 Variotherm process

Due to the fast freezing of the polymer melt when micro cavity filling, the mould temperature in micro injection molding process is normally higher or close to the glass transition temperature or soften temperature of polymers, shown in Fig2-5.

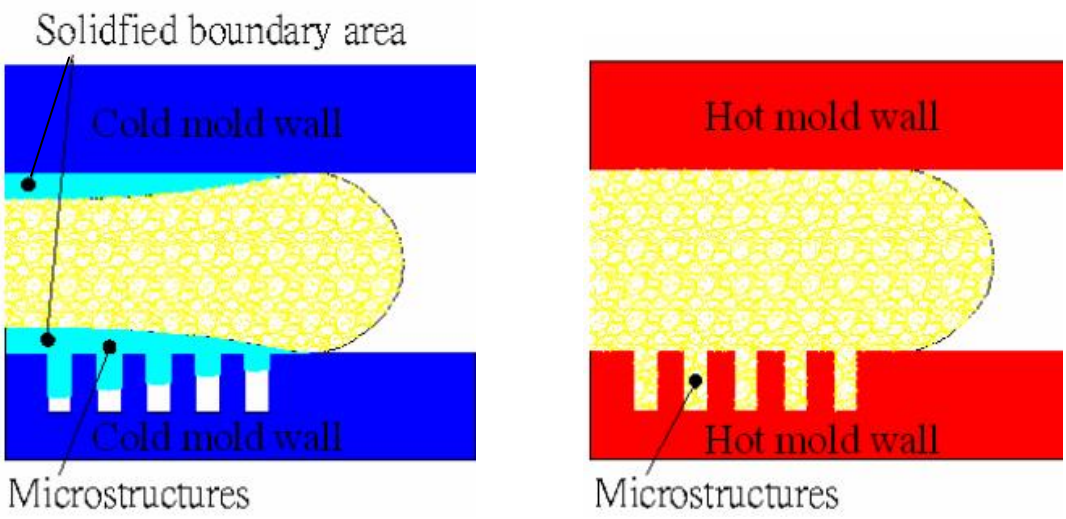


Fig.2-5 The reason for the variotherm system in micro injection molding

Therefore, during the micro injection molding cycle, the mould temperature needs to heat up to a high level and then cool down to the ejection temperature. A system able to rapid heat/cool the mould temperature is highly recommended to minimize the increased cycle time due to the high mould temperature as micro injection procedure. This varying mould temperature system named as 'Variotherm'. The advantages of Variotherm system are numerous, such as:

- Increasing the ability of high aspect ratio micro structure filling;
- Lower injection molding pressure and speed;

- Permit polymer or polymer composites with higher viscosity to be successfully applied for micro injection molding;
- Control the cooling speed of the melts so that it can reduce the residual stress and warpage of the micro structured parts;
- Concerning the final products, some defects like weld lines, short shot could be improved.

Many meaningful research results have been reported about different kinds of variotherm process, such as low thermal inertia mold with multi coating layers and cooling by liquid media, inductive heating, electrical resistance heating with cooling by liquid cold media and so on, shown as Fig.2-6.

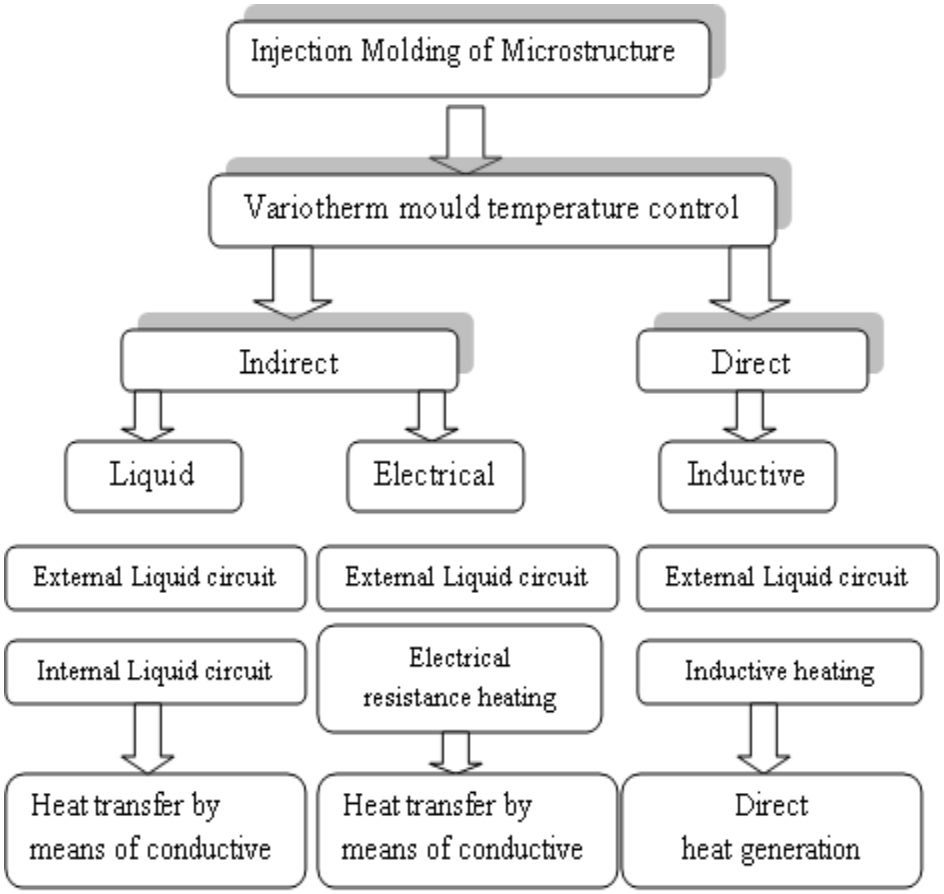


Fig.2-6 Main variotherm concepts used in micro injection molding process

For multi layer molds, in order to control the surface temperature of the mold rapidly, B.H.Kim and N.P. Suh developed one mold which consists of a woven graphite fiber fabric as a heating element, RTV silicon rubber as an adhesive, and a plasma sprayed ZrO2 layer on the mold surface as a moderate thermal insulation [69]. Based on this multi-layer mold concept,

other different researchers did more deeper and systematical investigation about matching the thermal and mechanical properties between the layers [70, 71]. In particular, Yao and Kim [71] used two materials with closely matched thermal and mechanical properties for mold construction, and they were able to use the mold for minimizing birefringence and residual stress in injection-molded parts. An ultimate solution to the thermal mismatching problem, however, would be a mold made of a single metal. Xu et al. presented a mold design with a low thermal inertia by employing air pockets inside the mold. These air pockets function as thermal insulations and thus a separate thermal insulation layer can be eliminated [72].

For inductive heating, the first patent on inductively heating injection molds was assigned to Wada et al. [73] 20 years ago. In inductive mold heating, an electrical coil passing high-frequency current is placed near the mold surface to induce eddy current in the mold. Due to the so-called skin effect [74] at high frequency, the resulting Joule heating is confined at the mold surface. One benefit of this method, therefore is, that the electrical insulation right beneath the mold surface is not needed. The major drawback of the inductive mold heating method, however, is due to the employment of the coil. Because direct embedment of the coil inside the mold is difficult, the common practice is to use a separate external coil. The reported experiments were thus limited to mold preheating before the mold closes. Furthermore, the coil needs to be carefully designed to achieve uniform surface heating. The method recently proved to be very useful in micro injection molding applications according to the experimental results of W.Michaeli from IKV RWTH Aachen, T. Benzler and V. Piotter et al. from IMF III Karlsruhe, and W.Schenkoethe and H.Kueck et al. from IKKT and IZFM of University Stuttgart [75–78].

For electrical resistance heating, N. H. Loh et al. designed and fabricated a variotherm mold based on this method for micro powder injection molding study. Results show that the variotherm unit is very useful for the high aspect ratio micro structure replication [79]. L. Xie and G.Ziegmann built a series of experimental mold with the same concept variotherm unit for weld line investigation in micro injection molding [80-85]. C.K.Wang et al [86-87], K.F.Zhang and Zhen Lu[88], Shimizu T et al [89] also constructed the micro injection mold with the electrical resistance heating method and did much research about the formability, morphology and mechanical properties of the micro injection molded parts with pure polymers and filled polymers.

There are still some other variotherm concepts which were presented but not widely applied, like oil heating/cooling, gas heating/cooling etc. Among them, there is one novel and promising concept reported by Dong Yao, which is based on the proximity effect between a pair of mold inserts facing each other with a small gap and forming a high-frequency electric loop, shown in Fig.2-7 [90].

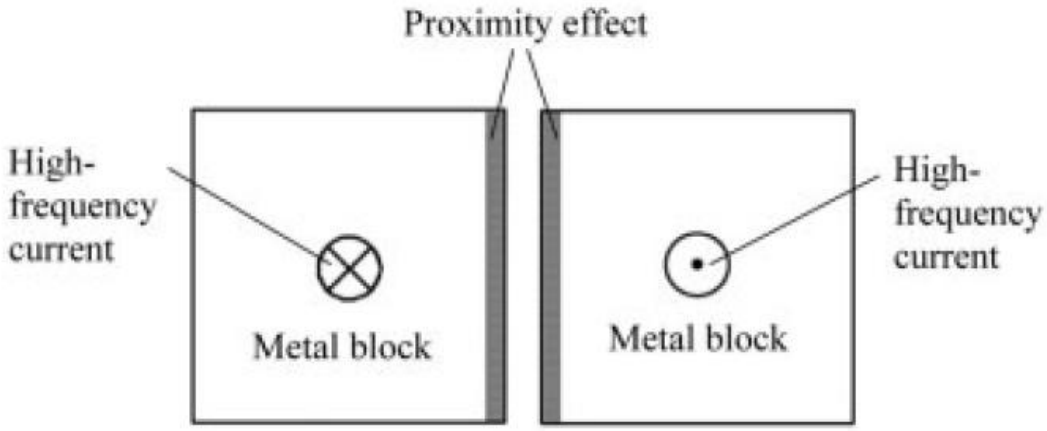


Fig.2-7 Principle of high-frequency proximity heating

As it was previously seen, the variotherm system is convinced to be a practical solution in micro injection molding. However, this system is still in developing and mainly be found in academic research application. Its application should consider the energy consuming of heating and cooling mould, as well as the mould geometry and investment.

2.2 Weld line

Weld lines are formed during mold filling whenever two separated melt streams recombine. This occurrence is caused by holes, inserts in the cavity, multiple gates variable wall thickness where hesitation or race tracking occurs. The weakness of mechanical properties and surface appearance defects due to weld line, are unfavorable in injection molding parts, especially in micro injection molding process.

There are two main types of weld line: one is the cold weld line (also named as knit line) and the other is the hot weld line (also named as meld line), shown in Fig.2-8a and b. Cold weld line is formed when separate melt fronts running in opposite directions meet. Hot weld line occurs if two emerging melt fronts flow parallel to each other and create a bond between them.

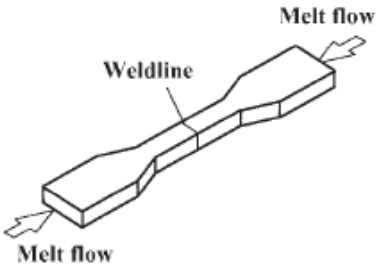


Fig.2-8a Cold weld line

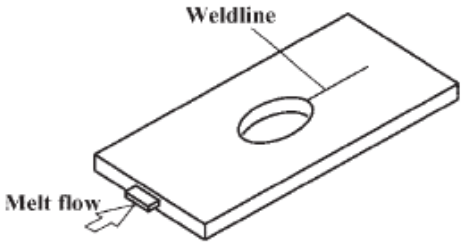


Fig.2-8b Hot weld line

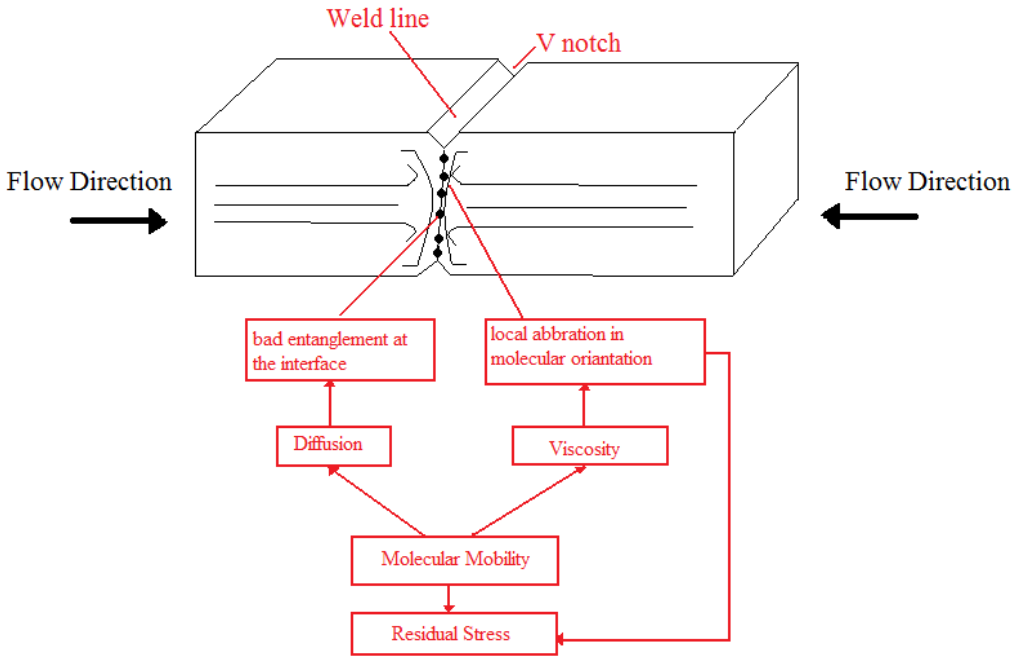


Fig.2-9 Reasons for lower mechanical properties in weld line region found from macro weld line research[92]

The low mechanical properties in weld lines are considered to be caused by several factors such as poor intermolecular entanglement across the weld line, molecular orientation induced by fountain flow, and the stress concentration effect of surface V-notch and so on, showed in Fig2-9.

The strength of weld line can reach 10% - 90% as strong as the originally used neat polymer materials. There are many factors relating to weld line's quality, which can roughly be classified as the following:

- Factor related to part design
  e.g. wall thickness of the part
- Factor related to mold design
  e.g. distance to the gate, gate size, cross section shape

- Factor related to processing condition
  e.g. melt temperature, mold temperature, flow front temperature, injection speed or injection/packing pressure
- Factor related to material
  e.g. type and dimension of the filler (fiber or particle)

Since weld lines often result in reduced mechanical strengths and poor optical surface appearance of injection molded parts, there have been a great number of investigations about the effect of processing conditions on the weld lines. Based on those research achievements, which are mainly focusing on the normal size injection parts (dimension scale is not less than 2 mm), one found out that improved thickness of the wall of the part leads to higher weld line strength; large gate size and shorter distance between gate and weld line cause a better quality of the weld line; Processing parameters normally are proportional to the strength of weld line in the material processing window. In addition, filling the polymer with fibers make the weld line more week than the pure virgin material due to the high orientation of fibers in the flow front, but the filler of particles enhance the weld line tension strength because of the connection effect of the particles when two flow fronts meet each other.

2.3 State of the art for investigation of weld line properties in injection molding process

Many achievements and research programs have been run and are still ongoing about weld line development, but most of the effects are concerning on normal size injection molding parts. These research results are processed by simulation or by experimental methods. As to the simulation for weld line forming in injection molding, Tham Nguyen-Chung presented a non-isothermal simulation of the weld line formation due to collision of two flow fronts [91]. This way the aforementioned sources of the weld line weakness and their interrelationship can be investigated with regard to the flow history and the thermo rheological situation, which as a whole enables a better understanding of the mechanisms of the weld line formation. I.S.Diaranieh et al[92] discussed the sensitivity of Moldflow® weld line prediction algorithm to variations of materials property and variations of processing conditions, and demonstrated that the average viscosity can be potentially used to predict the strength in regions influenced by weld line. Tham Nguyen-Chung, Christa Plichta, Gunter Mennig investigated the flow disturbance in polymer melt behind a obstacle and simulated this process by FIDAP®, those results are according to Moldflow® results and experiments [93]. A number of commercial simulation software are also available for predicting the position of

the weld line, like Moldflow®, C-Mold®, CADMOULD®, SIGMASOFT® etc, but they do not consider the detailed information in advancing melt front, such as fountain flow, surface tension and wall slip phenomena. These software systems can give the accurate results of macro injection molding parts, but not sufficient to do the precise simulation about weld line forming in micro injection molding process. However, some papers have an application to use the macro commercial simulation software in the micro scale case. V.Poitter etal. simulate the filling phase of multimode fiber connector ferrule and get a qualitative prediction for weld line[94].W. N. P. Hung et al simulate weld line away the gate during a micro gear (150μm, 1:1 aspect ratio)injection molding process by Moldfow [95].

The weld line development is investigated in experimental methods as well. In order to reveal the real forming process and find out various factors to affect the weld line properties, many tests and experimental methods are used. Generally processing parameters, materials properties, morphology of the vicinity of weld line and the stress concentration due to V notch in weld line surface etc, are regarded as the effect factors to weld line strength. In addition, tensile test, flexural test, impact test, single/double edge notch test, micro hardness test and compact tension tests have been taken to describe the strength of the weld line; especially tensile test is the most common measurement.

Turnag et al[96] did some research on how the processing parameters affect the weld line strength and microstructure of injection molded microcellular parts, using tensile test describing weld line strength. The results imply the changes in shot size brought about more significant changes in the weld-line strength, the weld line strength is seen to increase with shot size, melt temperature and injection speed. For HDPE material, Chang and Faison investigated the effects of processing conditions on the weld line strength of ASTM D638 sample part, and results showed that melt temperature is the most important effect parameter [97]. Koster compared the strength of sample parts with the same shape, but one is with weld line, the other one without, and results show that the residual stress and melt temperature have strong influence on weld line strength [98]. Kuehnert and G. Mennig used microhardness technique to characterize the quality of the weld line in injection-molded tensile bars and reveal the processing temperature affects the broadening of the weld line through the conditions for effective mutual interdiffusion of chains from the two fronts coming from opposite sides[99].Chang Lu et al investigated the ultrasonic improvement of weld line strength of injection molded PS/HDPE blends part and found the ultrasonic is an effective method to improve the entanglement of polymer molecular structure[100].

Kilwon Cho et al studied the strength of weld line in molecular level by compact tension method and compared the test results with tensile test, which imply that the compact tension test is more appropriate for measuring the interfacial adhesion strength across the weld-line, which excludes the notch effect[101]. Jin Kon Kim et al compared the strength of cold weld line between the neat PBT and PBT filled with fibers, the results show the fibers orientation near the weld line is paralleled to the weld line direction reducing the weld line strength dramatically[102]. D.F.Mielwski investigated the effect of additive in PP on weld line strength, and implied that the additives can improve the strength of weld line [103]. Kim and Sul built up a mathematical model to calculate the strength of weld line through regression experimental method, which is the function of melt temperature [104].

In addition to the research of weld line focusing on the macro scale parts, only a few papers concern with the micro scale weld line. W.Michaeli, H.Klein, J.Schulz, A.Spennemann, C.Ziegmann etal, investigated in machine and process development for micro engineering and developed microtensile testing machine using injection molded microtensile specimens of a suitable design, the minimum dimension of the microtensile testing specimen is D=1mm[12]. Cheng Hsien Wu and Wan Jung Liang, studied the strength of cold weld line in dumbbell sample with various dimensions crosssection, the minimum dimension of cross section is 0.3 mm×0.3 mm. The optimizing parameters to get the highest strength of weld line were attained [13]. G. Tosello et al investigated the relation between processing parameter and weld line formations both in the two-dimensional (direction and position) and three-dimensional range (surface topography characterization), based on a special micro cavity mold. Results showed that shape and position of weld lines are mainly influenced by mold temperature and injection speed [105-106].

The following conclusions could be drawn after reviewing the assigned literatures:

a. Many investigations have been done, focusing on the weld line issue of standard size injection molding, and little attention on the weld line developing in micro injection molding.
b. As to injection molding micro scale parts, the wide and comprehensive research attend to be done about which factors are the main poles affecting the weld line mechanical properties, why these factors can influence the weld line forming, and how the weld line strength can be improved through optimizing these factors.
c. The micro melt flow behavior during weld line developing process needs to be studied deeply, since the frozen layer at the micro channel wall should produce totally different

effects on the forming of micro weld line.

d. Comparisons of weld line properties in micro parts for neat polymer as well as filled polymer should be investigated, such as nano filled polymer composites.

Since nowadays the research on weld line in micro injection molding is relative limited, the proposal concentrating on exploring the weld line forming theory in micro scale is necessary and emergent.

3 Research goals and dissertation organizing concept

As the literatures cited and described in the chapters before, the fact is obvious that there have been numbers of research works on normal size injection molded weld line properties; however the study on the weld line formation and mechanical properties in micro injection molding conditions are relatively limited. Therefore, regarding to the developing theory of micro injection molded weld lines, many opening problems are still remaining to be solved, which are listed in the following partly:

- How the processing conditions affect weld lines strength;
- How the processing parameter influence the melts flow behavior in micro cavities, which are finally related to weld line strength;
- How the fillers in polymer composites influence weld line strength;
- What is the relation between the mould cavity geometry, runner system structure and weld line strength;
- Which modifications need to be done for the mathematical model and boundary conditions in order to simulate the weld line formation in micro injection molding process;

etc.

Those issues can be classified into three aspects, namely processing conditions, mould design and structures, and external processes. The goal of this thesis is heading towards the solution of three general aspects problems. Hence, some detail topics in each aspect are selected and investigated, then finally composed of this thesis. The solution strategy and dissertation organizing concept are charted in Fig.3-1.

In Chapter 4 the general experimental and test methods are explained, at the same time the processing materials, namely PP, PP/TiO2/CNF are also illustrated; Topics related to processing conditions are gained in Chapter 5 and 6 separately. Chapter 5 describes the relation between processing parameters and weld line strength; Chapter 6 concerns how the nano filler influence the weld line mechanical properties. The two topics involved in mould design and structure aspect are displayed in Chapter 7 and 8, which are focusing on the

correlation between gate dimensions, micro channel cross section shape and weld line strength; As for the final external process aspect, the effects of ultrasonic oscillation and metal coating layer on weld line strength are investigated in Chapter 9 and 10. Finally Chapter 11 discusses the melt filling and weld line forming process in the micro cavity by visual experimental method and numerical simulation.

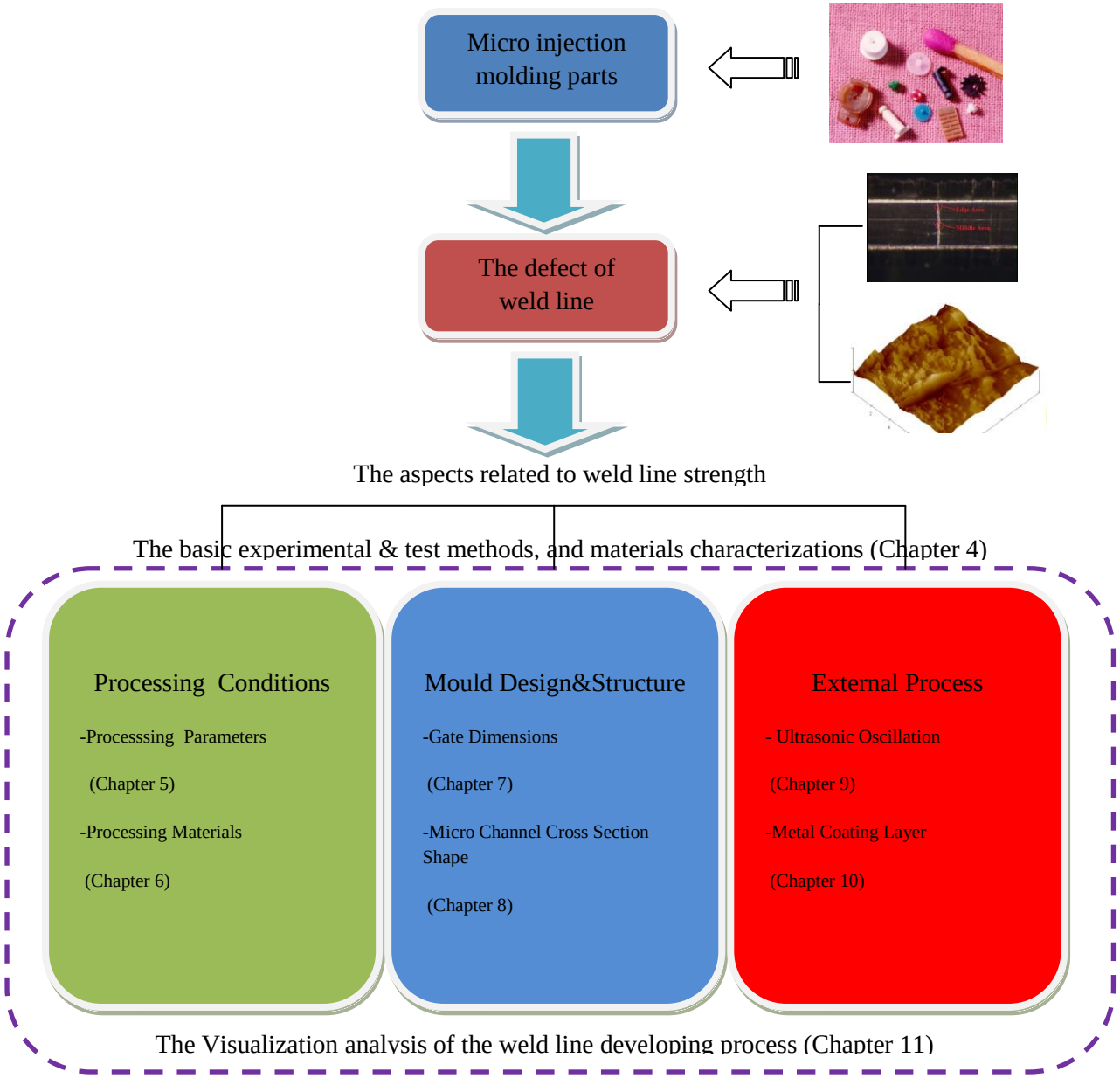


Fig.3-1 Solution strategy and dissertation organization

4 Characteristic methods and processing materials

In the following chapters, towards the aim at characterization of the materials properties and weld line strength, many analysis and experimental methods were applied. The basic principles underlying these methods and equipments are introduced briefly and generally.

Characteristic Methods

4.1 Thermal properties measurement

Thermal properties analysis is very important role for filled and unfilled polymeric materials characterization accounting for their melting temperature, thermal degradation temperature and crystallization temperature which in turn are essential specifics for guiding the initialization and configuration of related micro injection molding process parameters during experimental research.

4.1.1 Differential Scanning Calorimetry (DSC)

DSC is a thermal analytical method where the heat flux difference due to the chemical or physical transition of a sample can be detected as a function of temperature during the measurement of heating/cooling the sample at a certain defined rate of temperature with the comparison of the required heat amount of a sample and reference. Throughout the DSC testing, the sample and reference are maintained at nearly the same temperature.

Generally, the typical program for a DSC analysis is implemented as that a sample holding pan and a reference pan which should made of a material with the well original heat capacity are heated/cooled linearly as a function of time. The difference of heat flow changing between the sample pan and reference pan is obtained. Based on this measuring concept, the DSC curves of heat flux versus temperature or versus time can be patterned, as shown in Fig4-1. Normally, there are two different heat conventions, endothermic (heat absorbing) and exothermic (heat releasing) conventions. This curve can be used to calculate enthalpies of

transitions by mathematical integration calculating of the endothermic/exothermic peaks which can be expressed using the following equation:

$$\Delta H = KA \tag{4-1}$$

Where, ΔH is the enthalpy of transition, K is the calorimetric constant, and A is the area under the curve.

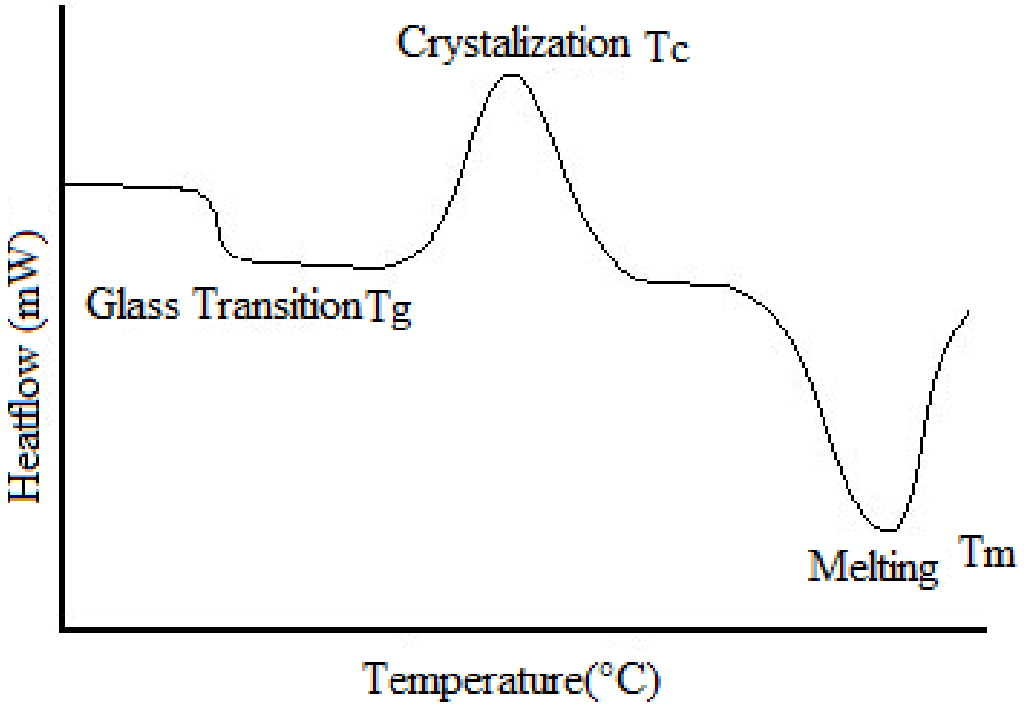


Fig.4-1 A schematic DSC curve demonstrating the appearance of several common features

As the curve is showing, DSC can be used to measure many characteristic properties of a material quantitatively and qualitatively, such as glass transition temperatures (T_g), melting temperature(T_m) and the crystallization temperature (T_c) as well as the crystalline degree for crystalline materials.

In this thesis, the DSC measurement is used to determine the melting temperature, crystalline temperature and crystalline degree of PP and PP nano filled composites. The apparatus is TA Instrument DSC2920. The measurement was carried out with a nitrogen atmosphere and a sample weight of 10±2 mg. Hermetically sealed sample containers were used in these experiments to avoid oxidation. The measurements were processed by a heat-cool-heat cycle. The sample was firstly heated up to 280°C from room temperature at the heating speed of 10°C/min, then was cooled down to 50°C at the same temperature speed in order to record the crystallization process of the sample. Afterwards, it was heated up to 280°C again at heating speed of 10°C/min aiming to track the melting behavior of the sample.

4.1.2 Thermogravimetric Analysis (TGA)

TGA is a well known measuring method to determine characteristics of materials through testing the changes of weight of samples as a function of temperature and/or time, such as degradation temperature, the filler's concentration in matrix, absorbed moisture contents of materials and so on. TGA instrument commonly comprises with a high-precision balance assembled a pan (normally made of platinum) loaded with the sample. During the measurement, the pan is heated linearly in a small electrically heated oven integrated with a thermal sensor to precisely control the temperature. The weight variation of the sample is measured by the precision balance and recorded by the control unit of the instrument. Finally, one TGA curve of weight versus temperature/time can be obtained.

TGA testing method is served in this thesis to verify the concentration of the nano fillers in polymer composites prepared by the kneading process as well as to determine the thermal stability of PP nano filled composites with various nano fillers and concentrations. The measurement was carried out in a TGA apparatus from Hi Res TGA 2950 of TA Instruments. The sample was heated at Nitrogen atmosphere from room temperature to 650 °C at a heating rate of 10 °C/min.

4.2 Mechanical Property Characterization

4.2.1 Tensile test

The tensile test is the best-known test in material testing. It determines tensile strength, one of the most important properties of material. Furthermore, it is also possible to determine elongation at fracture as a toughness measurement of the material. In the tensile test, a mono-axial stress is generated in a material sample. This stress is induced via external loading of the sample in a longitudinal direction via a tensile force. There is then an eve distribution of direct stress in the test cross-section of the sample. In order to determine the strength of the material, loading of the sample is slowly and continuously increased until its fails.

The maximum test force occurring is a measurement of the strength of the material. The so-called tensile strength R_m, according to the equation (4-2), R_m calculated from the maximum test force F_B and the initial cross-section A_o of the sample, in Fig.4-2. The simplest way of determining the maximum test force is via the maximum pointer on the force display. In the tensile test itself, the cross-section of the sample is reduced, and the actual stresses are considerably higher.

$$R_m = F_B/A_o \qquad (4\text{-}2)$$

R_m is selected as the characteristic criterion for mico injected weld line strength in the presented study. The tensile tests were executed on the Zwick universal mechanical test machine. The distance between two sample holding crossheads was 13.8mm, and tensile

speed was 1mm/min. The tensile strength was recorded by the Testxpert® software automatically. In order to minimize the tolerance of the testing, the measurement was repeated 5 times for samples produced in the same batch and the final tensile test result was the average value of those 5 results.

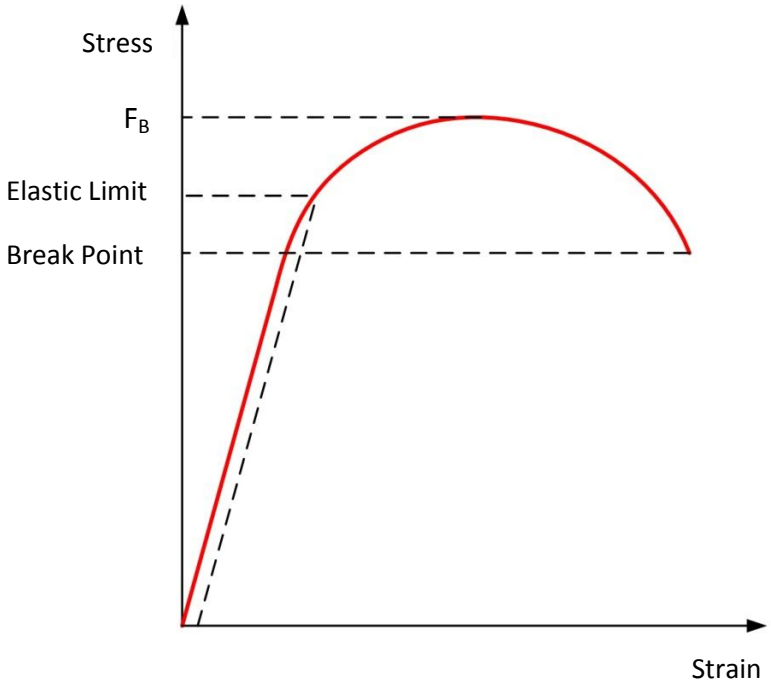


Fig.4-2 Tensile test stress vs. strain relation curve

4.3 Microscopic and morphology observation

4.3.1 Scanning Electronic Microscope (SEM)

The SEM is a quite usual morphology images producing method of electron microscope that produce the picture of the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern (normally range from a few hundred eV to 40 keV). The electrons interact with the atoms of the sample which can make the sample produce signals that undertake information about the sample's surface topography, composition and other properties such as electrical conductivity.

For conventional imaging in the SEM, specimens should be electrically conductive, at least on the surface. As for nonconductive specimens are therefore usually coated with an ultrathin coating of electrically-conducting material, commonly gold, deposited on the sample either by low vacuum sputter coating or by high vacuum evaporation.

There are two SEM apparatus, respectively from CamScan44 Cambridge Ltd and Evo 50 Zeiss GmbH., employed as the characteristic measurement to verify the nano fillers orientation in weld line areas and their dispersion situation in Polypropylene as well as the

morphology information in micro injection molded weld lines. The electron beam energy used in the measurements was ranged from 3 KeV to 20 KeV.

4.3.2 Atomic Force Microscope (AFM)

The key component of the AFM is the elastic cantilever with a sharp tip (probe). When the tip is very close to the test specimen surface, the weak force between the atom of the shape tip and the atom of the specimen (10^{-12}~10^{-6} N) will induce the cantilever elastic deformation, which is according to the Hook's law. Typically, during the measurement, the tip does raster scan on the test surface, and a constant contact force between the tip and the specimen surface is maintained. The deflection of the cantilever is recorded by using a laser spot reflected from the top surface of the cantilever into an array of photodiodes. Therefore, the profile and information on the testing sample surface can be finally displayed in a visual way. Fig.4-3 illustrates the principle of the ATM.

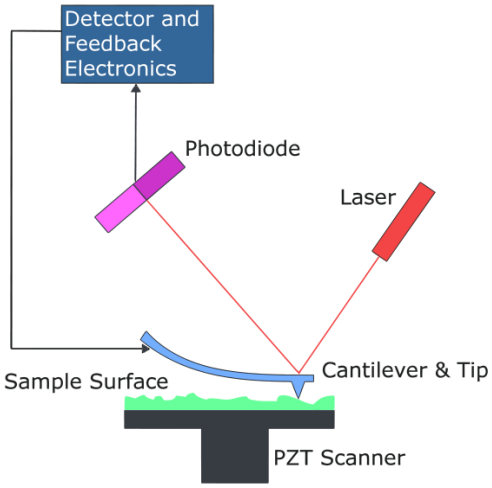


Fig.4-3 The schematic illustration of the AFM working concept[107]

4.3.3 Wide Angle X-ray Diffraction (WXRD)

X-ray diffraction techniques are based on the elastic scattering of X-rays from structures that have long range order, which means the materials are in crystal states. It is normally used to characterize the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline or powdered solid samples, is also commonly applied to identify unknown material substances, by comparing the obtained diffraction data with a XRD pattern database maintained by the International Centre for Diffraction Data.

Based on the measured intensity, angle position and bandwidth of crystal feature peaks in an X-ray diffraction test, the distance of crystal lattice and crystallite size can be calculated by the Bragg equation and Scherrer equation [108].

Bragg equation:

$$d_{hkl} = \frac{n\lambda}{2\sin\theta} \tag{4-3}$$

Where n is the diffraction level related to the form of crystals; λ is wavelength of the irradiation X-ray source; θ is the Bragg angle.

Scherrer equation

$$L_{hkl} = \frac{k\lambda}{\beta_{hkl}\cos\theta_{hkl}} \tag{4-4}$$

Where k is shape factor associated with the crystallites (assumed as 0.9 here); λ is wavelength of the irradiation X-ray source; θ is the Bragg angle and β_{hkl} is the half height of the feature peek (in radians).

By the X-ray scattering angle range, this technique can be clarified as wide angle and small angle X-ray diffraction, wide angle is concentrating on scattering angles 2θ larger than 5° and small angle is close to 0°. In the thesis, WXRD was implemented with Cu Kα radiation (λ=0.1541nm) (Simens D5000, Germany) to access the nano fillers' distribution in the polymer matrix according to their corresponding peek's intensity, scattering angle and bandwidth in the spectrum curve.

4.3.4 Polarized Light Microscope (PLM)

Polarized light microscopy can distinguish between isotropic and anisotropic materials by detecting the different refractive indices of the isotropic and anisotropic structures of material. Thus it can reveal comprehensive information related to the structure and composition of materials.

Micro injection molded plastic parts made of semi-crystalline polymers, like PP, normally composed of amorphous and crystalline material structures. Therefore, the PLM is one ideal instrument to help the researcher get the materials morphology distribution and growing situation in various directions, particularly in the observation of the polymer parts' section microstructures. Furthermore, through this method the information about the inner stress distribution near weld lines area could be collected as well.

4.4 Rheological property

Rotational rheometer and High pressure capillary rheometer

The rheometer is an instrument used to characterize the rheological properties (generally, viscosity v.s. shear rate) of materials in various status such as a liquid, suspension or slurry flows. It is normally not used for the Newtonian fluid testing which has constant viscosity at

a certain temperature. In contrast, it is well-defined for the non-Newtonian fluid measuring, especially for shear-thinning fluids like polymer melts.

There are several distinctively different types of rheometers depending on their different testing principles: Rotational rheometer, Processing rheometer and Capillary rheometer.

In the presented thesis, the high pressure capillary rheometer was chosen as the characteristic device for polymer and nano filled polymers, since the rheological information of materials at high shear rate situation are more interesting for us due to the high injection pressure and speed during micro injection molding process. The brief description of the capillary rheometer test can be explained as follows: the polymer granulates are poured into a capillary with constant cross-section and precisely known dimensions, then the capillary is heated to some aiming testing temperature (higher than polymer melting temperature). The fixed pressure drop or flow rate is driven by the mechanical unit of the rheometer onto the polymer melts in the capillary. Under conditions of laminar flow, the flow rate related to shear rate and pressure drop related to shear stress are measured and according to the dimensions of capillary, the flow rate can be converted into a value for the shear rate and the pressure drop into a value for the shear stress. Varying the pressure or flow allows a viscosity versus shear rate curve to be determined.

In this study, the rheological property was characterized by a high capillary rheometer from Goettffert GmbH (Rheograph 75) with max.force 75KN. The nozzle used in the measurement has 15mm length, 1mm diameter of outlet hole and 90 degree feeding angel, the rheological testing was executed only on one single capillary without the second reference capillary, and the testing results were corrected by the Rabinowitsch equation.

4.5 Visualizing experimental device

High speed camera

The recording system for weld line developing is a high speed camera with video/image processing software (HSC 1000P). The recording speed of the high speed camera was set as 923 fps and picture size is 1024×768 pixels.

Processing Materials

4.6 Thermoplastic

Two kinds of thermoplastics were applied as the experimental processing materials, which are PP (PPH 734-52 RNA) produced by DOW Europe. GmbH and HDPE (LUPOLEN5031L) produced by Basell GmbH. The general properties of the used PP and HDPE are listed in Table 4-1. In order to understand the processing ability and execute the initial simulation, the

rheological properties of the PP and HDPE were measured by the rotational rheometer and high pressure capillary rheometer. Results can be found in Fig.4-4.

Table 4-1 General property of PP and HDPE used in this study

Properties	PP	HDPE
Density (g/cm3)	0.9	0.952
MFR(g/10min)	52 (230°C/2.16kg)	6.5 (190°C/2.16kg)
Tensile Stress (MPa)	37	37.7
E modulus	1240	1050
Heat Deflection Temperature (°C)	105 (0.65MPa, unannealed)	-
Viscat Softening Temperature (°C)	152	125
Melting Temperature(°C)	165	131
Specific heat capacity [J/(g .°C)]	2.62 (126.85°C)	-
Thermal conductivity [W/(m .K)]	0.2067 (125°C)	-

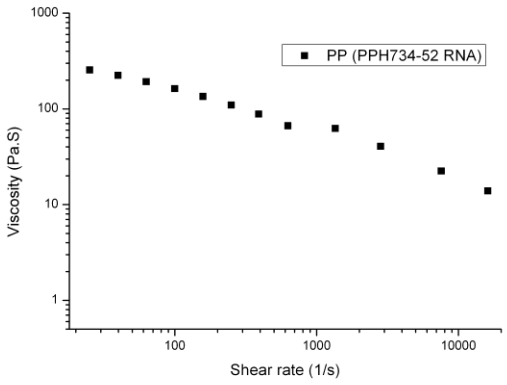


Fig.4-4a Viscosity vs Shear rate of PP (PPH 734-52 RNA) at 200°C

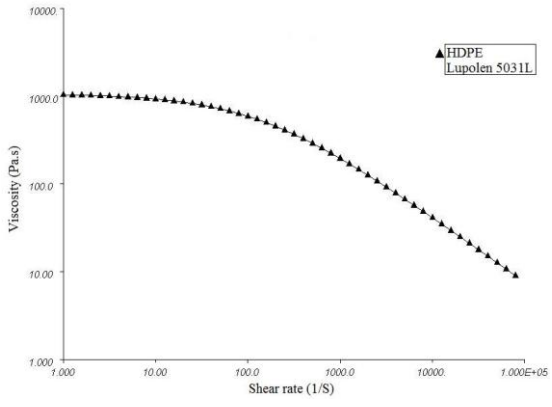


Fig.4-4b Viscosity vs Shear rate of HDPE (Lupolen 5031L) at 200°C

4.7 Nano fillers

4.7.1 Carbon Nano Fibers (CNFs)

Carbon nano fibers are a form of vapor-grown carbon fiber which is a discontinuous graphitic filament produced in the gas phase from the pyrolysis of hydrocarbons. Currently, the CNFs have been developed to Pyrograf-III from the original Pyrograf-I. On commercial market, Pyragraf-III is available as PR-19 and PR-24 in 3 different grades. They are AG (as grown CNF), PS (pyrolytically stripped CNF), and HT (heat treated CNF). PR-19 has fiber diameters of 100 to 200 nm and fiber lengths of 30-100 micron. PR-24 has fiber diameter of 60- 150 nm and fiber lengths of 30 to 100 micron. The CNFs used in this study are purchased from the company *carbon NT&F **21***®, which belong to HT (heat treated) PR-24. The basic properties are list in Table 4-2. The SEM image of the CNFs bundles is shown in Fig.4-5.

Table 4-2 Properties of the CNFs applied in the study

Properties	**Values**
Purity (%)	>90
Diameter (nm)	60 - 150
Length (μm)	30-100
Amorphous carbon (%)	<5
Ash (catalyst residue) (%)	<2
Special surface area (m^2/g)	~20
Thermal conductivity (W/ m·k)	<2000
Tensile strength (GPa)	~7.0
Tensile modulus (GPa)	~600
Density (g/cm^3)	2.1
Electrical resisitivity (micro Ω·cm)	~55

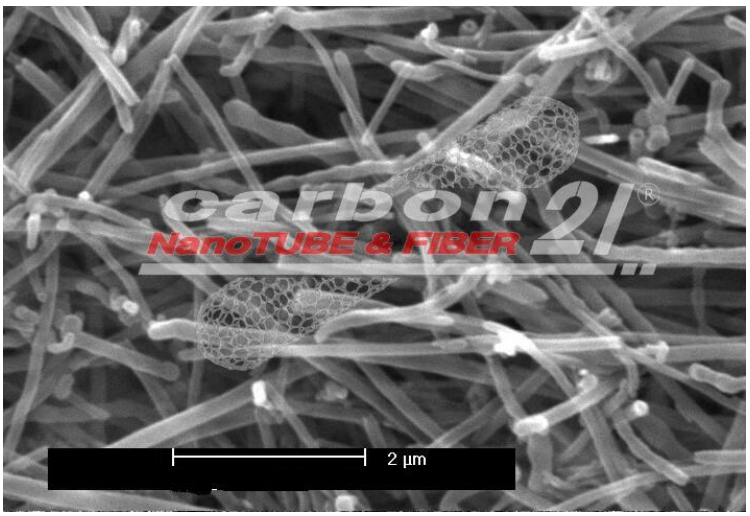


Fig.4-5 SEM image of the Carbon Nano Fiber used in the study

4.7.2 TiO2 Nano Particles

Titanium dioxide occurs in nature as well-known minerals rutile, anatase and brookite, The most common form is rutile, which is also the most stable form. Anatase and brookite both convert to rutile upon heating. Rutile, anatase and brookite all contain six coordinated titanium. The Tio2 nano particle is the most widely used white pigment because of its brightness and very high refractive index (about 2.7), in which it is surpassed only by a few other materials. Additionally, it is also used as practical additives for polymers in order to satisfy with the applications consisting of high-voltage insulation, IC substrate boards, toners fluorescent tubes, toners, battery separators, and UV sun screen lotion.

The TiO2 nano particles used in this dissertation are Hombitec RM produced by the Sachtleben Gmbh, which are spherical with about 20 nano meter diameter and 4 g/cm3 density. Fig.4-6 shows a TEM micrograph of TiO2 particles at excessive agglomeration.

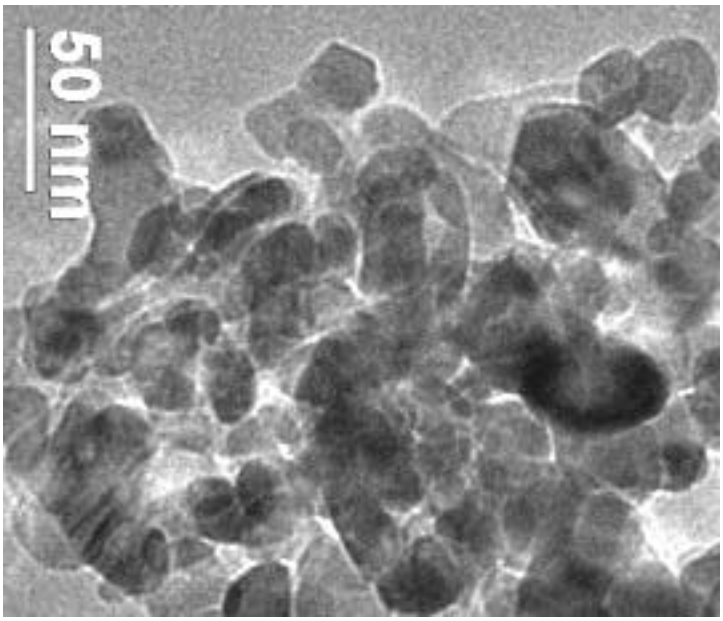


Fig.4-6 TEM image of the TiO2 nano particles used in the study

4.8 Composites compounding

Twin screw kneader

There are two kinds of processes served as the compounding methods for filled polymer composites, namely high shear method and low shear method. High shear method refers to extrusion process, and low shear method normally represented by kneading process. Extrusion process is external mixing which is not effective to the dispersion of the nano particles in polymer matrix. Kneading is internal compound offering flexile and controllable compounding time, which is advanced to get homogenous composites.

By the number of screws and their rotational directions, the kneader is generally classified as co-twin screw kneader and co-triple screw kneader, schematically shown in Fig.4-7. In the presented study, a Thermo Haake® co-twin screw micro kneader was applied as the Nano composites compounding equipment, which can supply 6 temperature control zones in mixture chamber up to 360°C and a maximum torque 5cNm, 48cm^3 chambers. The appearance of the kneader is displayed in Fig.4-8.

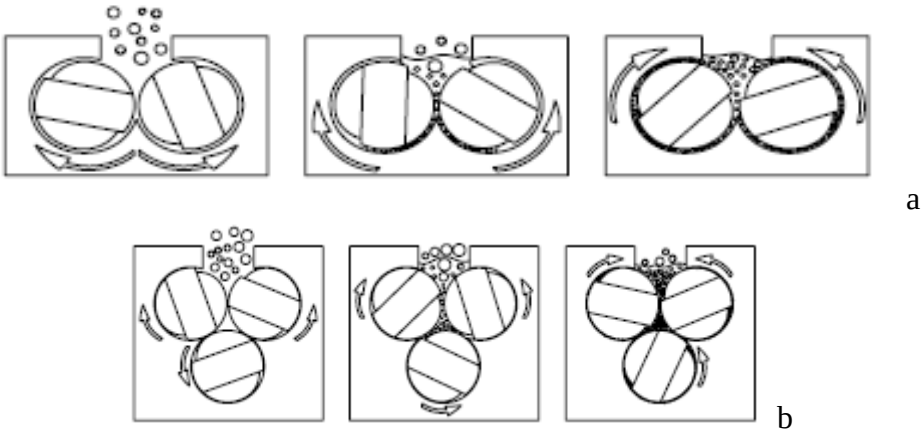
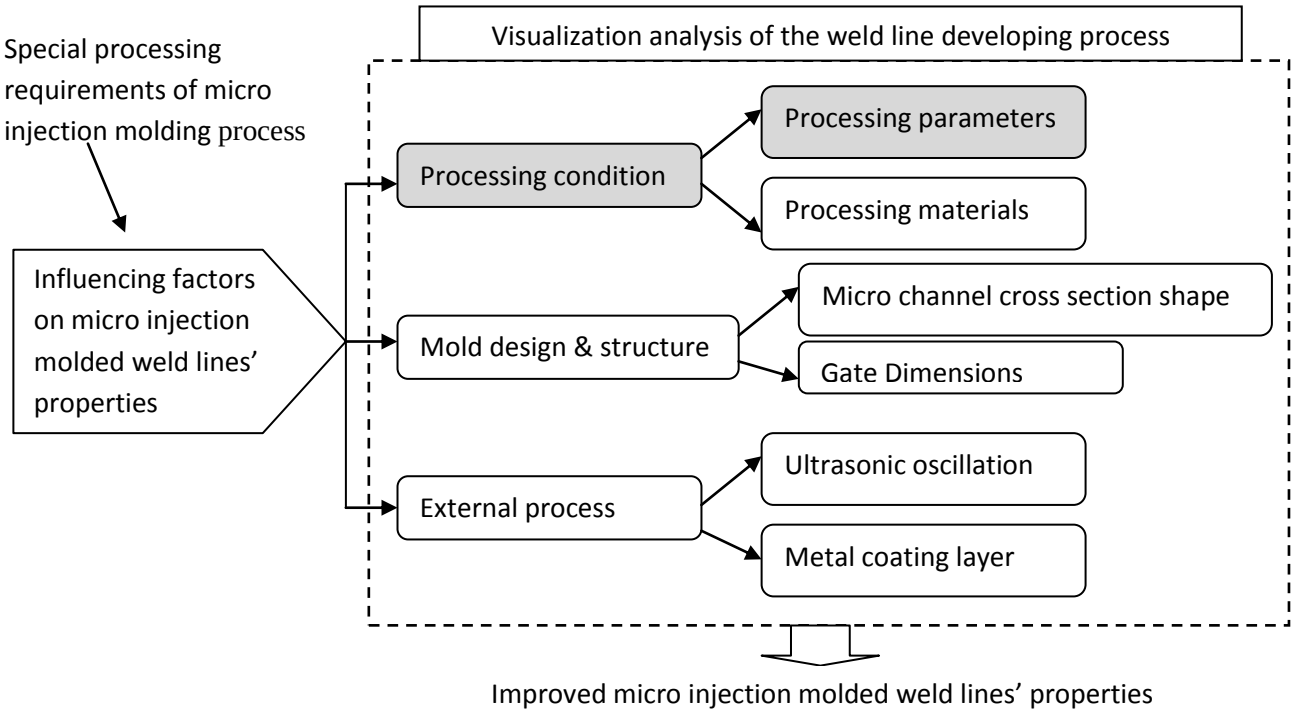


Fig.4-7 Schematic figure for the screws assembling and moving in co-twin screw kneader (a); co-triple screw kneader (b)[118]

Fig.4-8 the Thermo Haake Polylab co-twin screw kneader

Researching Concept Implementation and Evaluation



Processing Condition Factor I

5 Effect of processing parameters on weld line mechanical properties

Injection molding processing parameters are close related to the weld line's mechanical properties, since they are the main direct factors influencing the polymer morphology, molecular orientation and entanglement in weld line forming process. Within this chapter will mainly investigate the correlation between micro injection molding processing parameters and weld line strength.

5.1 Experimental principle and setup

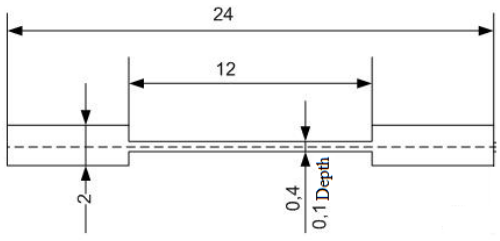
5.1.1 Principle

A micro scale tensile specimen was chosen as the objective micro injection molded part. Based on this part, one double-gate single micro tensile sample cavity injection mold was designed and fabricated, which is integrated with a variotherm unit. Micro injection molding experiments were performed at different processing conditions in accordance of the L18 (3^7) orthogonal experimental table. Then the molded micro tensile samples were measured by tensile test machine in order to determine the strength of the micro injection molded weld line. Finally, by the Taguchi experimental method, the relation between processing parameters and weld line strength was analyzed; the influencing significant sequence of the parameters on weld line strength and the optimized processing parameters level was obtained.

5.1.2 The part and injection mould

The specimen is a micro scale dog bone tensile test sample. The geometry and dimension of the specimen is illustrated in Fig.5-1. During the process, the polymer melts flow into the cavity from two ends of the micro tensile specimen, finally there is the intended weld line is formed in the middle of the specimen. The whole length of the tensile specimen is 24mm and the length of test area is 12mm. The cross section shape is rectangular with the dimension of 0.1(depth) mm ×0.4(width) mm.

a.



b.

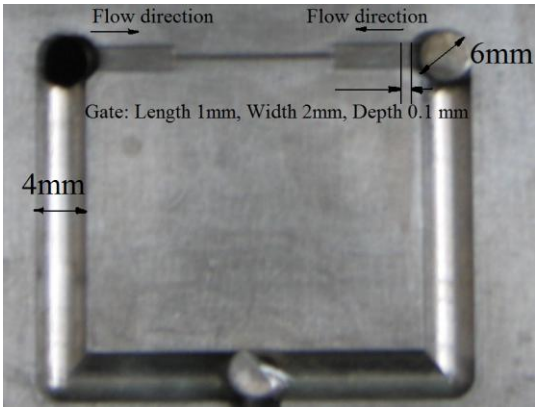


Fig.5-1 a. Specimen geometry and dimensions(mm);b. the cavity location and runner system arrangement in the real case

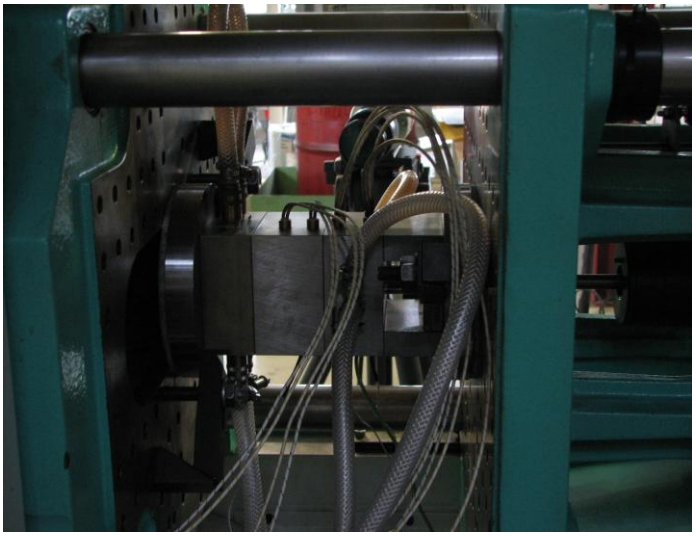


Fig.5-2a Variotherm system with heating pipes and cooling channels

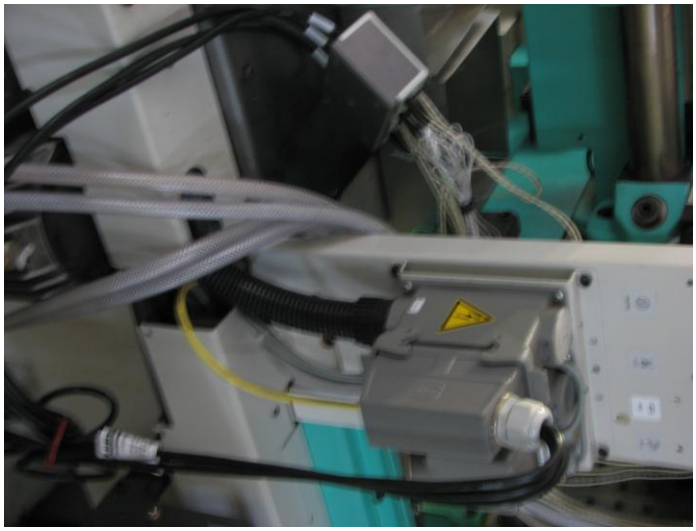


Fig.5-2b The controlling connection interface between heating pipes and the injection molding machine

A mould integrated with variotherm system was designed and constructed, shown as Fig.5-2a. In the variotherm system, the high power electrical heating pipes realize the rapid heating requirement, which is directly connected with the injection molding machine and close loop controlled by the machine's system, presented in Fig.5-2b. As the cooling media, cold water channels (at 19°C) undertake the responsibility of rapid cooling.

5.1.3 Experimental Plan

Experiments were carried out by the Taguchi experimental method, which could be used to find out the significance of processing factors for the mechanical properties of the weld line in micro injection molding and give an optimal processing parameters option for the best quality of weld line.

According to the introduction about the micro injection molding process cycle in the chapters discussed before, there are 6 important processing parameters to be selected as the objectives, which are melt temperature, mold temperature, injection speed, injection pressure, packing pressure and ejection temperature. Due to the nonlinear influence of these factors, 3 levels are assigned for every factor. And based on the levels of the factors, a L18 (3^7) orthogonal table is be applied in the design experiments. With the help of initial experiments, levels of factors are selected more reasonably and reliably, which are listed in Table 5-1.

Table 5-1 Factors and Levels in the Taguchi Experiments

Factors	1	2	3
A Melt Temperature/℃	210	230	250
B Mold Temperature/℃	120	140	160
C Injection Pressure/Mpa	500	1000	2000
D Packing Pressure/Mpa	400	800	1600
E Ejection temperature/℃	40	60	80
F Injection Speed/ cm^3/s	60	80	100

In analysis of Taguchi experimental method, the signal-to-noise (S/N) ratio usually is introduced, which is able to describe the power of a response signal divided by the power of the variation in the signal due to noise. The maximization of the S/N ratio causes minimization of any property that is sensitive to noise. In weld line mechanical property study, the largest strength is expected. So "larger- the- better" characteristic S/N ratio is applied in the analysis, which is calculated by equation (5-1):

$$S/N = -10\lg\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right) \tag{5-1}$$

Where y_i is the experiment result, and n is the number of samples for each experimental trial. In this analysis way, the level of factor with larger S/N ratio means this level can lead to larger strength of the weld line in micro injection molding.

Additionally, the relative contribution of each control factor to the overall experimental aimed result is also able to be calculated by Taguchi experimental method. Then the significant order of factors will be obtained.

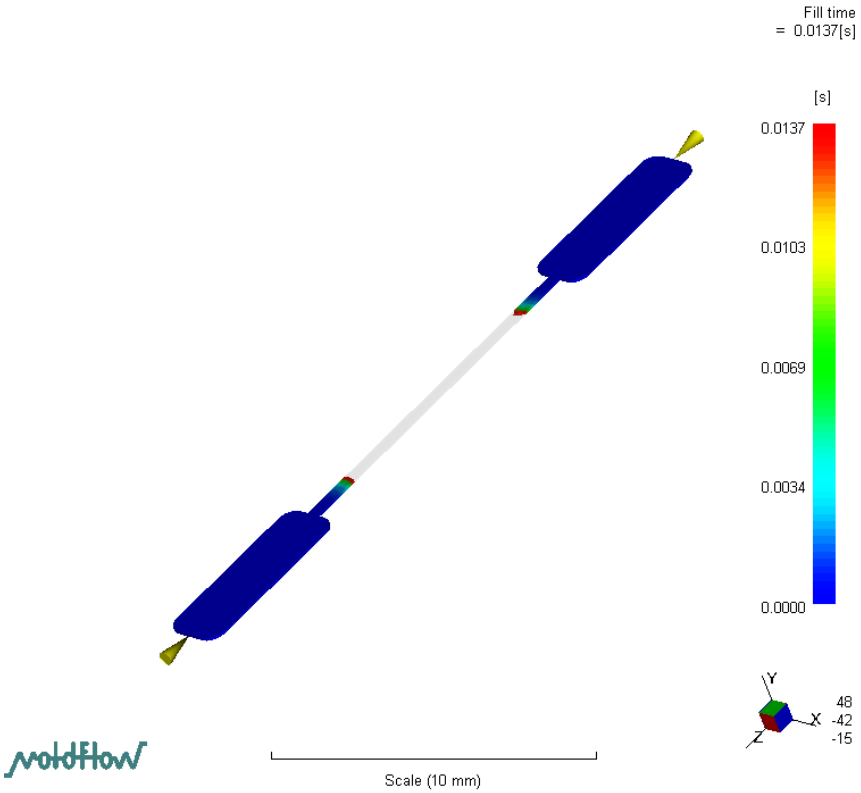
Finally, according to the orthogonal results obtained in the experiments, using multiple regression method, the relation formulation between micro weld line's strength and processing parameters could be set up based on the Chebyshev orthogonal polynomial.

The injection molding experiments were carried out on a horizontal injection molding machine (Arburg® 320C). The machine offers a maximum clamping force 600 KN, maximum injection pressure 2500 bar and the screw diameter of 30 mm. The processing material is Polypropylene (PPH 734-52 RNA) mentioned in the previous chapter.

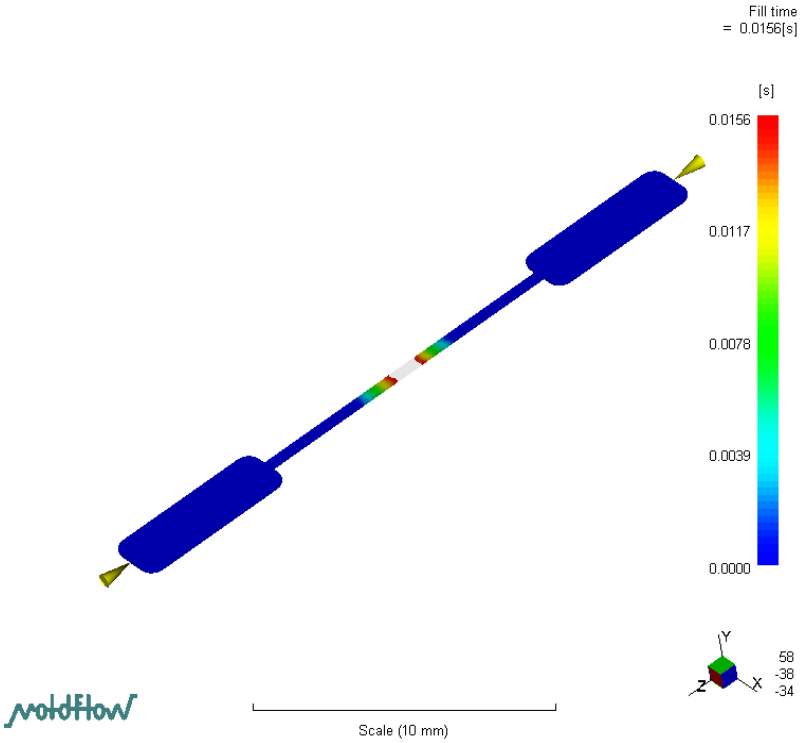
5.2 Correlation between processing parameters and weld line strength

5.2.1 Initial simulation

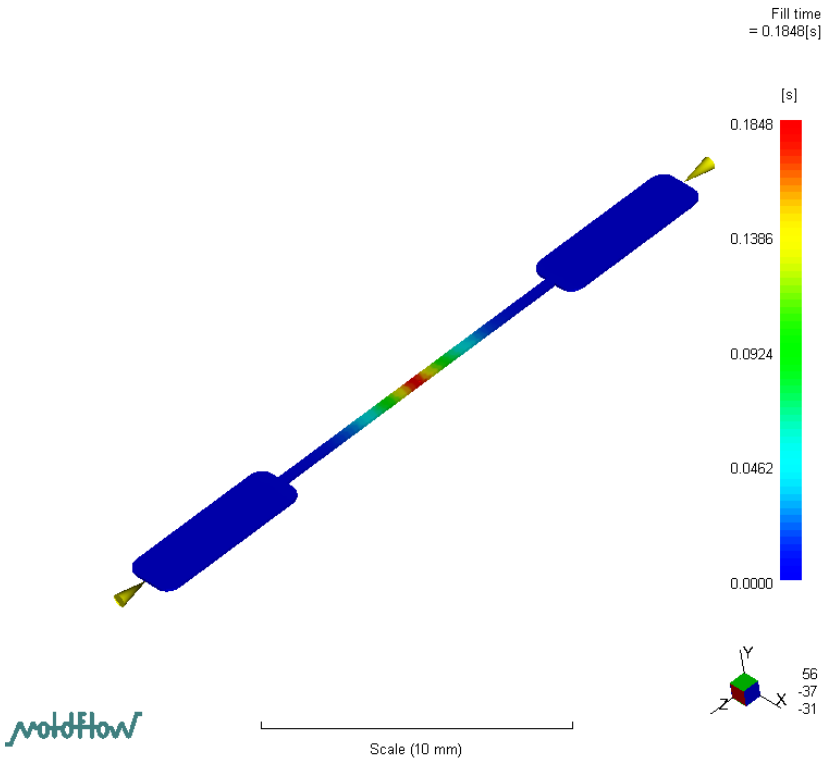
Before the real orthogonal experiment starts, the filling simulation and some initial experiments were carried out. From simulation results performed by MoldFlow MPI5.0® and presented in Fig.5-3, it could be figured that when the mold temperature is not high enough (lower than 120°C), the micro specimen cavity cannot be completely filled, even if the highest injection pressure (2500 bar) was used. That is related to the fast freezing problem for polymer melts flowing in micro scale cavity. But when the mold temperature reaches 120°C, even at relatively low injection pressure, the complete filled specimen still can be produced. The results were also verified by the real injection molding experiments. The initial testing "short-shot" and complete filled specimens are shown in Fig.5-4.



a. melt temperature 210 ℃, mold temperature 80 ℃, flow rate 60 cm^3/s, injection pressure 150 MPa

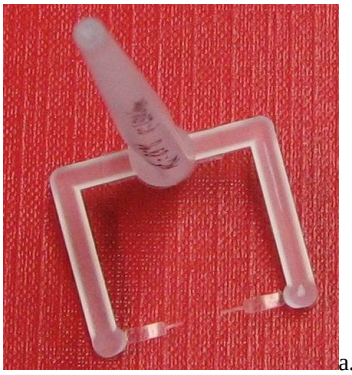


b. melt temperature 210 ℃, mold temperature 100 ℃, flow rate 60 cm^3/s, injection pressure 250 MPa



c. melt temperature 210 ℃, mold temperature 120 ℃, flow rate 60 cm^3/s, injection pressure 50 MPa

Fig.5-3 Filling simulation results in different processing conditions, in **a. b.**, the micro tensile cavity cannot be completed filled; in **c.**, the sample can be completely filled


a.

b.

Fig.5-4 a Short shot of micro specimen, Injection pressure=2500 bar, Mold Temperature=85°C
Fig.5-4b Full filled micro specimen, Injection pressure=500bar, Injection speed=20 cm^3/s, Mold Temperature=120°C

Table 5-2 L18 (3^7) orthogonal table and the final weld line strength of samples

Experiment Nr.	T melt[℃]	T tool[℃]	Inj.Pressure [bar]	Post Pressure[bar]	T_{Demold} [℃]	Injection Speed[cm3/s]	Tensile Strength[Mpa]
1	210	120	500	400	40	60	38.798
2	210	140	1000	800	60	80	33.948
3	210	160	2000	1600	80	100	21.044
4	230	120	500	800	60	100	32.129
5	230	140	1000	1600	80	60	15.588
6	230	160	2000	400	40	80	14.203
7	250	120	1000	400	80	80	13.077
8	250	140	2000	800	40	100	14.982
9	250	160	500	1600	60	60	17.840
10	210	120	2000	1600	60	80	23.123
11	210	140	500	400	80	100	31.263
12	210	160	1000	800	40	60	19.659
13	230	120	1000	1600	40	100	33.861
14	230	140	2000	400	60	60	22.949
15	230	160	500	800	80	80	22.170
16	250	120	2000	800	80	60	25.849
17	250	140	500	1600	40	80	14.376
18	250	160	1000	400	60	100	21.217

Aiming to solve the problem of rapid heating and cooling issues, the variotherm system was applied during the process, the mold temperature was heated up to 120°C fast, and the specimen could be completely filled, even in the low injection pressure and injection speed.

According to these initial orientation experiments, the reasonable factor levels of processing parameter could be set down in the following orthogonal experiments.

5.2.2 Signal-To-Noise(S/N) Analysis

The micro tensile specimen with weld lines were prepared by injection molding process, according to the L18 (3^7) orthogonal table. Then the specimens are under material tensile load tested by a universal test machine (Zwick GMbH), and the ultimate strength of samples is the test aim. The crosshead moving speed is 1 mm/min and the clamping interval is 13.8mm applied for the test. For constant processing conditions, the experiment samples tensile test is repeated 5 times, and the average value of these 5 results is regarded as the final result. The final ultimate tensile stress measured results are shown in Table5-2. By the equation (5-1), the S/N ratio of every factor level will be calculated. This method used by the Taguchi analysis is to quantify the average responsibility for each individual control factor level. Fig.5-5 shows how the processing parameter effect on the weld line strength and tells which factor level will lead to highest weld line strength.

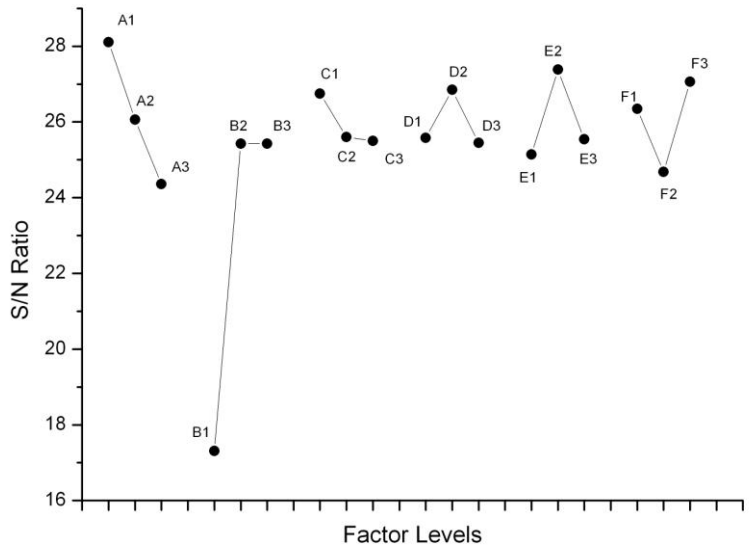


Fig.5-5 Processing parameters levels S/N ratio

5.2.3 Processing parameter effects mechanism analysis

From Fig.5-5, there is a negative effect for higher melt temperature (Factor A) in influencing micro weld line strength. This is an unexpected result and in opposite to the results obtained in Macro scale weld line study. In past research works about macro weld lines; it is usually

believed that higher melt temperature causes better ultimate stress of the weld line because higher melt temperature is helpful for diffusion of polymer molecules in weld line area. It also might lead to higher material degradation, which is an unfavorable phenomena in the process because the material degradation process involves stress enhanced absorption and concentration of the chemical molecules at susceptible microstructural sites. These will induce bad mechanical properties. While in this study on micro weld line, Factor A gives an opposite relation between melt temperature and weld line strength. That can be explained as in micro scale part injection molding process, the negative influence of higher temperature is larger than positive. That is, in micro scale due to the tiny dimension of cavity, the effect of melt temperature on the entanglement extent among polymer molecules can't be exerted as well as in macro scale, meanwhile its effect on the material degradation is same as in macro scale.

The performance of higher mold temperature (Factor B) is positive for weld line strength. Higher mold temperature means higher weld line strength, but the S/N ratio in 140°C and 160°C are same, which illustrated when the mold temperature is higher than 140°C, the weld line strength will not be improved by higher mold temperature.

As for injection molding pressure (Factor C), and packing pressure (Factor D), the results are unexpected. However, since the strength of weld line is related to many complicated factors and decided by various conditions, further research works have to be done in the next step.

Ejection temperature (Factor E) represents the effect of cooling process on the strength of weld line. The lower ejection temperature will make the frozen layer thicker on weld line, which means more area can not be connected between two flow fronts nearby the wall area around V-notch. In contrast, the higher ejection temperature will give a "soft connection" after the meeting of two flow fronts, which will lead to reduced mechanical properties finally. Therefore, the best micro weld line strength is achieved in the middle level of ejection temperature (60°C). Its S/N ratio is obviously better than under and upper levels.

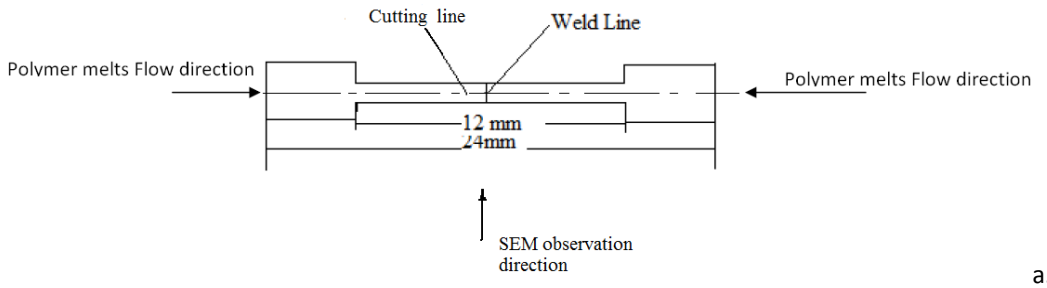
Injection molding speed (Factor F), which is related to shear rate of flow melt, will influence the orientation of polymer molecular during melt filling phase. When two flow fronts encounter together, the orientation of molecular structures is a main factor for the strength of weld line. The orientation normal to flow direction contributes to a bad entanglement of molecules, while the orientation parallel with flow direction gives a good connection when the molecular chains meet each other. Higher injection molding speed leads to higher shear rate and shear stress, which helps get better quality weld line. However, when the injection molding speed is not high enough to make the molecules of two directions orient almost ideally parallel with flow direction, the contact area and chance will be decreased between molecules from both directions. It is unfavorable to micro weld line strength. That's why the experimental results show the weld line strength in 80 cm^3/s (middle level) is even lower than 60 cm^3/s (lower level). And when the injection molding speed reaches a much higher level in 100 cm^3/s (upper level), the weld line strength is enhanced again.

5.2.4 Significant sequence analysis

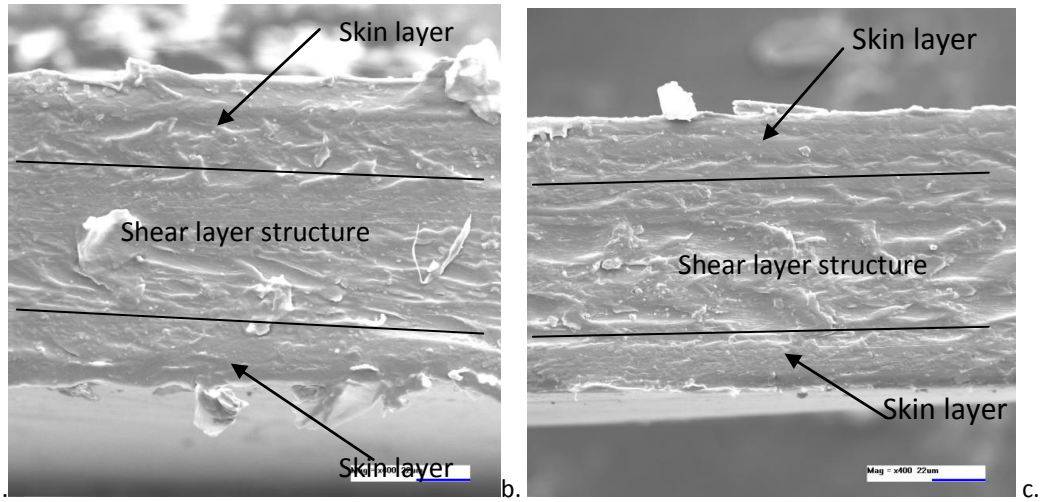
In Taguchi experimental analysis, the extreme error analysis and S/N ratio analysis is combined, the analysis of variance (ANOVA) can be performed, and then the significance order of parameters can be found depending on the contribution to weld line strength of each factor. The results described in Fig.5-5, in which the fact can say mold temperature's contribution (Factor B) is 42.4%, melt temperature's (Factor A) is 19.59%, Injection molding speed's (Factor F) is 12.43%, Ejection temperature's (Factor E) is 11.7%, Packing pressure's (Factor D) is 7.31% and Injection pressure's (Factor C) is 6.53%. So the significant order is BAFEDC, the factors related to temperature are the main influencing part for weld line strength, effects of factors related to pressure are decreased. But packing pressure is more important than injection pressure in this weld line strength improving case.

5.2.5 Morphology structure analysis in weld line area

Based on the analysis and results about the relation between processing parameter and weld line strength and the discussion of their function mechanism on weld line strength, further investigations were performed in order to find the original reason why the mechanism works in this way. Morphology structure near weld line area was firstly studied because the way that processing parameters affect weld line strength is based on their impacts on the morphology structure of materials. The photos observed under SEM show the morphology structure of the materials along the thickness direction of the sample area near weld line (in Fig.5-6), there are only skin layer and shear structure and no core layer like normal size injection molding parts (in normal size injection molding process parts, the core layer occupied the main portion of the material microstructures). This kind of morphology structure in micro injection molding is more easily affected by the processing condition. The thickness of skin layer is sensitively related to temperature condition, and the shear structure is closely related to injection speed. This result verified the conclusion obtained before, which presents mold temperature and melt temperature play most important role in deciding the weld line strength, and followed by injection speed.



a.



. b. c.

Fig.5-6 **a**. Schematic drawing for Microtrom cutting and SEM observing direction; **b.** and **c.** Morphology structure in micro sample middle weld line area observed by SEM (400×)

5.2.6 Micro weld line strength prediction

According to Taguchi Analysis, injection pressure and packing pressure are rarely affecting strength of weld line during the micro injection molding process, so the prediction formulation is only based on the other four parameter factors neglecting influence of pressure. As for the orthogonal experiment method, the Chebyshev polynomial is usually used to be the base formulation of regression analysis. After calculation and analysis, it was found that the quadratic order of the formulation in this case is not significant. So the prediction formulation is regarded as a first order polynomial. The coefficients of 4 variants can be calculated by the Chebyshev polynomial coefficient equation, and the final formulation obtained is described below, equation (5-2):

$$F_{weldline} = 50.403 - 0.0573T_{melt} - 0.1038T_{tool} - 0.0039T_{demold} + 0.00828V_{Inj} \qquad (5\text{-}2)$$

In order to check the precision of the prediction formulation, two other confirmation experiments were made, and the comparison between real test results and prediction results is listed in Table.5-3

Table.5-3 Confirmation Experiments Results

Confirmation Experiments	Test Results (MPa)	Prediction Results (MPa)	Error Percent
1	30.75	24.56	20.13%
2	28.579	25.54	10.64%

The 1st experimental processing parameters are T melt=220℃, T tool=130℃, Inj.Pressure=2500bar, Post Pressure=2000bar, T_{Demold}=40℃, Injection Speed=50 cm3/s; the 2nd experimental processing parameters are T melt=220℃, T tool=125℃, Inj.Pressure=300bar, Post Pressure=240bar, T_{Demold}=50℃, Injection Speed=110 cm^3/s.

5.3 V notch analysis of micro weld line

In this study, a long distance profile scan test machine is used to measure the weld line's V notch profile. The profile test of a V notch in the weld line's different area is executed and the comparisons are made among different weld line specimens with different size V notches. The scanning test was separately performed in a different area of weld lines, which is namely middle and edge areas of weld line, shown in Fig.5-7.

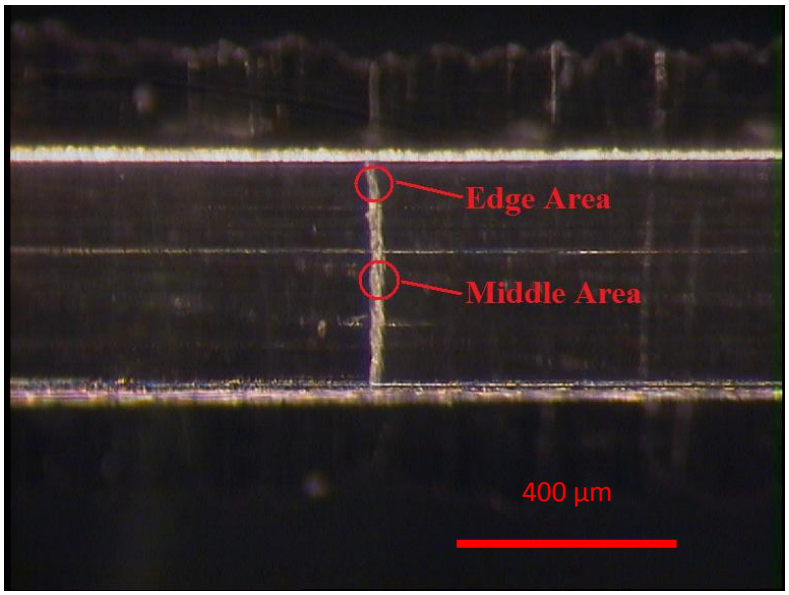


Fig.5-7 Scan profile testing areas for weld line V notch

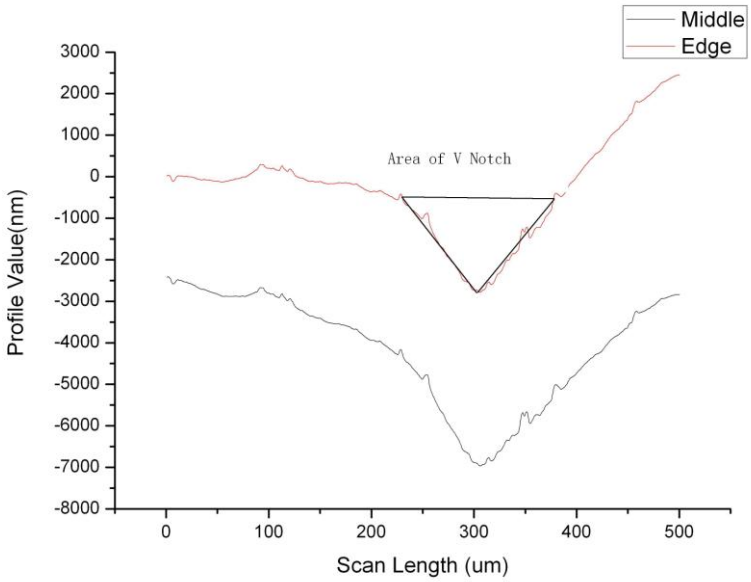


Fig.5-8 Weld line V notch profile scan test for Micro Weld Line Sample in T_{melt}=210℃, T_{tool}=140℃, Inj.Pressure=1000bar, Post Pressure=800bar, T_{Demold}=60℃, Injection Speed=80 cm^3/s, separately in middle and edge of sample.

Fig.5-8 shows that the V notch size in the specimens' middle surface is larger and deeper than in the edge and the surface height in the middle surface is lower than in edge. That can be explained as the frozen layer and shrinkage in middle part of specimen is larger than in edge part .However, based on the tensile test theory, it is confidential that the v notch in edge of specimen contributes more influence for decreasing the ultimate tensile test results. So the V notch profile in the edge of samples will be the main research point in this study.

The area of V notch is supposed as the evaluation of the size of V notch, shown as Fig.5-7. The relation between V notch size and ultimate tensile stress is studied, shown as Fig.5-9. By comparing the test results of experiment Nr.2, Nr.15 and Nr.12, it can be concluded that a smaller V notch area relates to a higher ultimate tensile stress of the weld line in micro injection molding.

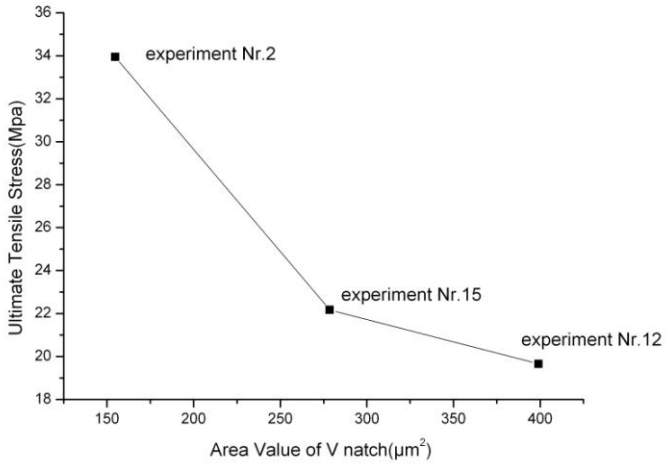
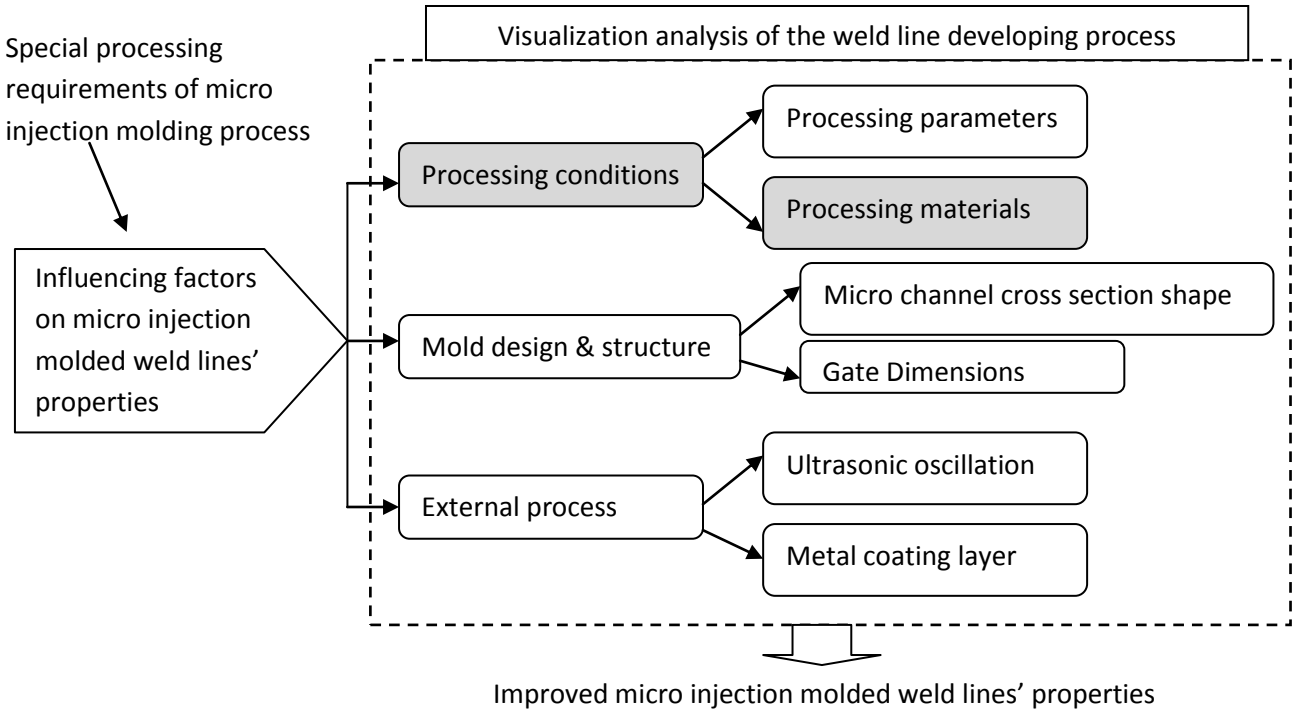


Fig.5-9 Relation between V notch Size and Ultimate tensile strength of micro injection molded weld line with PP

Summary

Based on a variothermal mold with visual structure, for PP material the relation between weld line strength and processing parameters in micro injection molding are found. The optimal processing parameters are obtained by Taguchi Analysis, which is $A_1B_2C_1D_2E_2F_3$ and the significance order of processing parameters influencing weld line mechanical properties is obtained, which is BAFEDC. Then through Chebyshev orthogonal polynomial, the four variants prediction formulation is set up for the micro injection molding weld line. The prediction errors are lower than 21%, checked by confirmation experiments. Additionally, effects of the V notch profile on weld line strength are also studied. The results show V notch size in the specimens' middle part is larger and deeper than in the edge and the surface height in the middle surface is lower than in edge. The smaller V notch area also leads to a stronger micro weld line similar to macro scale case.



Processing Condition Factor II

6 Effect of nano fillers on weld line mechanical properties with various fillers geometry and concentration

Many kinds of fillers are compounded with polymers in order to modify the thermal, physical and mechanical properties of the polymer matrix since several decades ago. Particularly in case of nano filled composites (nano particle or fiber with the scale from 1 nanometer to as large as 100 to 200 nanometers), due to the same magnitude between polymer coils and nano fillers, molecular interaction between the polymer and the nano fillers will give polymer

composites unusual properties that conventional polymers cannot possess[109-114]. With the appearance and development of micro injection molding process, this kind of amazing material is also applied in it for satisfying the special photonic, electrical, thermal and mechanical requirement of some smart functional micro system parts, e.g. fuel cell bipolar plate, micro fluid analytic plate and so on[115-118]. However, as the normal injection molding process, with various fillers geometry and contents, the weld line strength in micro injection molding process should be influenced differently as well. Therefore, the following chapter is focusing on the correlation between nano filler geometry, concentrations and micro injection molded weld line strength.

6.1 Experimental principle and setup

6.1.1 Principle

The micro tensile specimen and mould used in Chapter 5 were also applied in this study. Before the start of micro injection molding process, the polymer composites were prepared by compounding polypropylene and nano fillers (TiO2 nano particles and Carbon nano fibers) with different weight percents. Then in the same injection molding processing condition, the micro tensile samples with weld lines for each PP/Nano composites were formed. The tensile tests were served as the characterizing method for weld line strength. Comparison of the weld line strength responded to each composites, the influencing trend and relation between nano filler and micro weld line strength were revealed.

6.1.2 The PP/Nano composites preparation and characterization

Compounding

The PP/Nano composites compounding were carried out in a counter rotating kneader, which is shown and described in Chapter 4. In the preparation, with the various weight proportions, the polymer matrix PP and nano fillers were added into the kneader chamber in total amount of 40g each time. First, PP was put into the heated chamber and held at 190°C for roughly 2 minutes, then the nano fillers was fed into the chamber. After 15 minutes compounding of the matrix and filler at 60 rpm, the final composites were collected and granulated by a grinder for injection molding process in the next step. The Fig.6-1 shows the composites in the chamber after the single time compounding. Granulates of different kinds of nano composites to be used in micro injection molding process are displayed in Fig.6-2. Based on this process, the PP composites with 10%, 20%, 30% and 35% (by weight) TiO2 nano particle, Carbon nano fiber and hybrid TiO2/Carbon (1:1) were prepared.

Fig.6-1 The composites in the kneading chamber after compounding

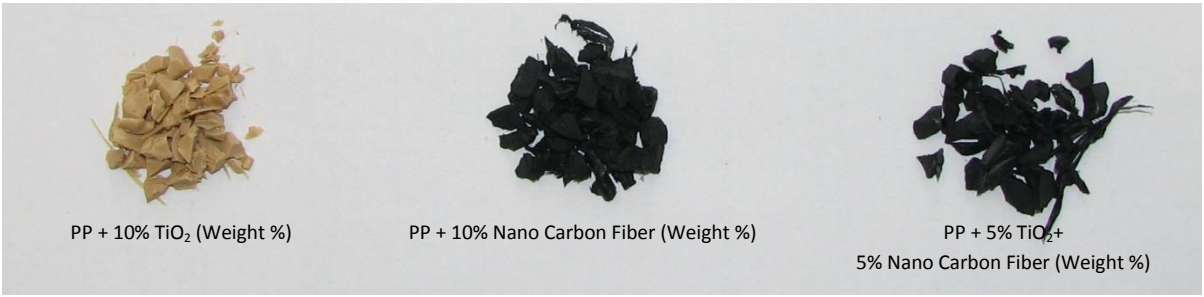


Fig.6-2 Granulates of the composites for injection molding process (nano filler 10% weight)

During the kneading procedure, the torque rheometer integrated in the kneader recorded the kneading response of the PP/Nano composites in different nano filler fractions, shown as Fig.6-3. With the fraction increasing of nano fillers, the torque for composites kneading is increased. Due to higher viscosity, composites with nano carbon fibers always need higher torque than composites with nano TiO2 particles. However, all the composites have the same trend in torque and time relation. At the beginning stage, the torque significantly increased when the pure granule nano fillers were fed into the chamber, then the torque dramatically decreased because the PP transited from solid to melt state completely and started to mix with nano fillers; After the peak, called as “loading peak” when the PP polymer begins to blend with TiO2 nanoparticles to produce a granule-dough stage, the feedstock then turned into dough stage and produced consistent properties. The torque was in a stable value, which

means a relative homogeneous feedstock was produced when consistent plasticizing properties were detected.

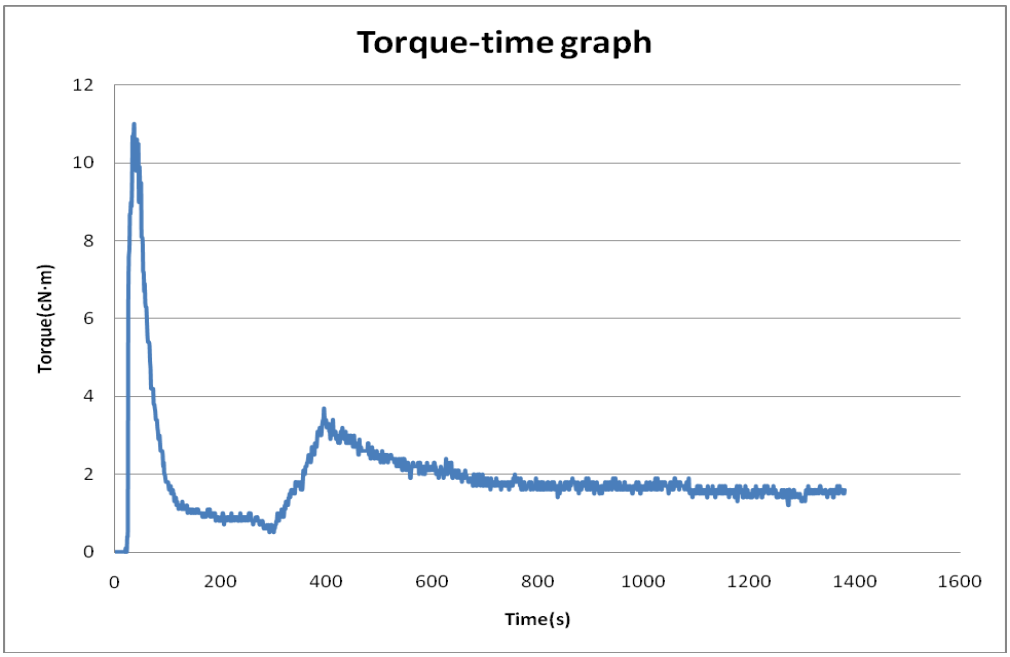


Fig.6-3 Torque versus time curve of the PP/Nano composites during kneading process (PP+10wt% CNFs)

Characterization

TGA

In order to verify and confirm the contents of nano fillers in PP matrix, all materials after compounding were measured by TGA. The results are shown in Fig.6-4, which indicate the tolerance of the nano filler contents is acceptable and the process for preparation of the composites is suitable and practical. Additionally, the information about the thermal stability of the composites is also able to be gained. With the both kinds of nano fillers (whatever TiO2 nano particle or Carbon nano fiber), the stability of the polymer are enhanced obviously. With increasing nano filler concentration, the thermal stability of polymer nano composites was getting better. In 10% level, PP with carbon nano fiber has best stability, PP with nano TiO2 is the next and the hybrid fillers lead to the lowest derivation temperature. But in 20% level, the hybrid nano filled PP composites have higher decomposition temperature, as the results from the enhancement of the cystallinity and more restricted molecular mobility due to the nano hybrid particle and fiber interfusion structures.

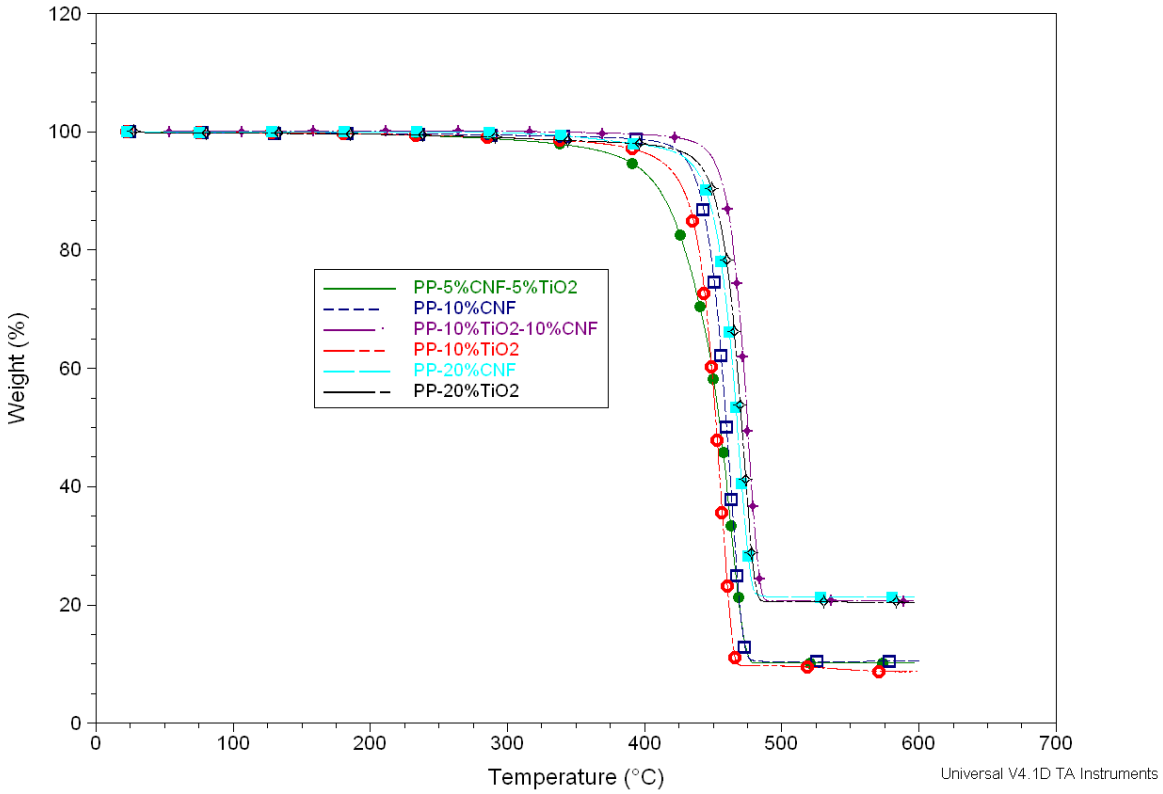


Fig.6-4 TGA measuring results of PP/Nano composites

WXRD

The WXRD measuring patterns of unfilled PP and nano filled PP composites are shown in Fig.6-5. The feature X-ray diffracting peaks of pure PP were displayed at 2θ= 13.88°, 16.64°, 18.61°, 21.02°, 21.56°, 25.2° and 28.48°, which are respectively corresponding to the (110), (040), (130), (111), (041), (060) and (220) diffraction planes of PP α-form crystal morphology. The feature diffraction peaks of Carbon nanofibers and TiO_2 nanoparticles are observed at 2θ=25.76° (CNFs) and 27.24°(TiO_2).

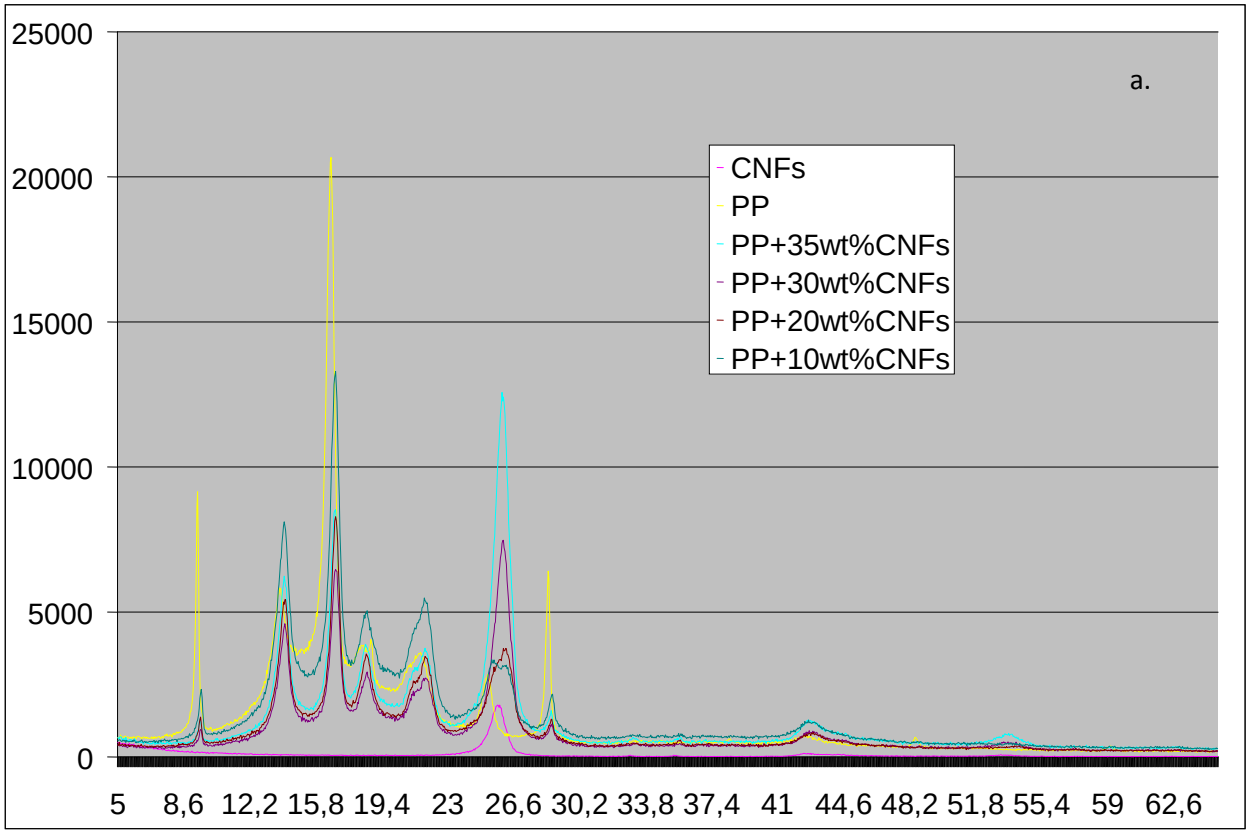
According to the XRD traces, the crystal form of PP was not changed after adding nano fillers, since there are no feature peaks appeared corresponding to β and γ form crystals of PP. However, with the addition of nano fillers, the position of the PP α-form peaks was shifted rightward to larger 2θ angle slightly, and the intensify of those peeks changed more or less.

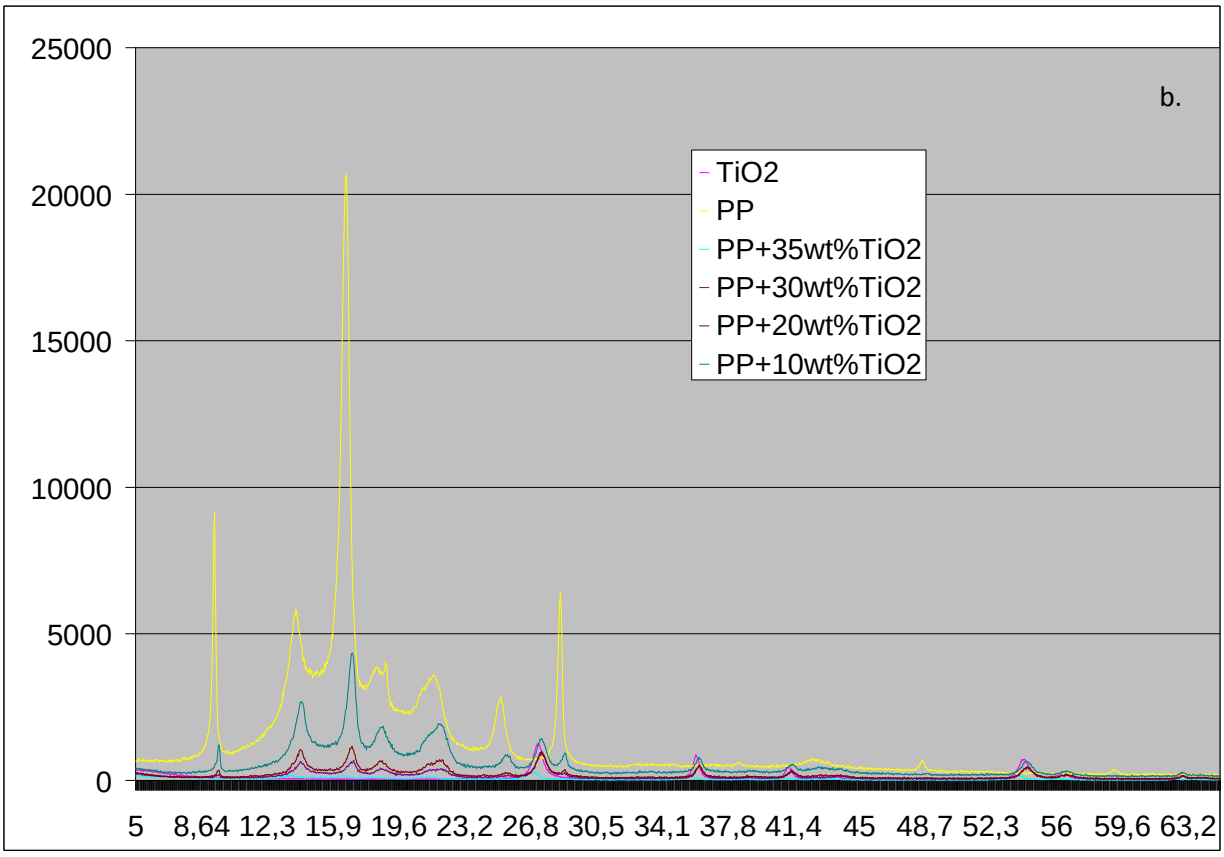
According to Bragger Equation (4-3) and Scherrer Equation (4-4), the fact based on XRD patterns can be found that with loading of CNFs and nano TiO_2 particles, the distance among the diffraction lattice planes of PP crystallites is slightly decreased in general. By adding 10 wt% CNFs, due to the increment of feature peak half height, the crystallite size of L_{hkl} perpendicular to the (110), (130), (111) and (041) plane are smaller than the those of pure PP. As the loading content of CNFs increasing, the crystallite size of those planes becomes larger

than the case of unfilled PP, but it becomes smaller again when the loading fraction reaches 35wt%. Meanwhile, the intensity of diffraction feature peaks corresponding to the (040) and (220) crystal plane of α form is decreased; the resulting crystallite size is larger than that of neat PP. One additional fact worth to be mentioned is that from 10wt% to 30wt% of CNFs, the intensity of all diffraction peaks for PP/CNFs composites is reduced with increment of the loading content, but it increases again at 35wt%.

Regarding to TiO_2 nano particles, with their addition in PP matrix, the intensity of all diffraction feature peaks for PP/TiO_2 composites are reduced gradually as the loading fraction increases, which means the crystallite size of α form in PP becomes larger.

Additionally, for all nano filled PP composites, new diffraction peaks near 2θ=25.76° and 27.24°, respectively corresponding to CNFs and TiO_2. For CNFs, the intensity of the feature peak is increased as the CNFs loading contents increase. The feature peak of α form in the plane (060) was replaced by the feature peak of CNFs after 10wt% due to the raising amount of CNFs. Furthermore, comparing with the pure CNFs, the feature peak of CNFs in PP/CNFs composite show higher intensity, which is proportional to loading contents. For TiO_2, only 10wt% of TiO_2 addition enhanced the intensity of its feature peak than that of pure TiO_2 nano particles. From 20wt%, the intensity of this feature peak starts to decrease and lower than the case of pure TiO_2, which means the larger crystallite size appear associated with the agglomeration of the nano particles in polymer matrix.





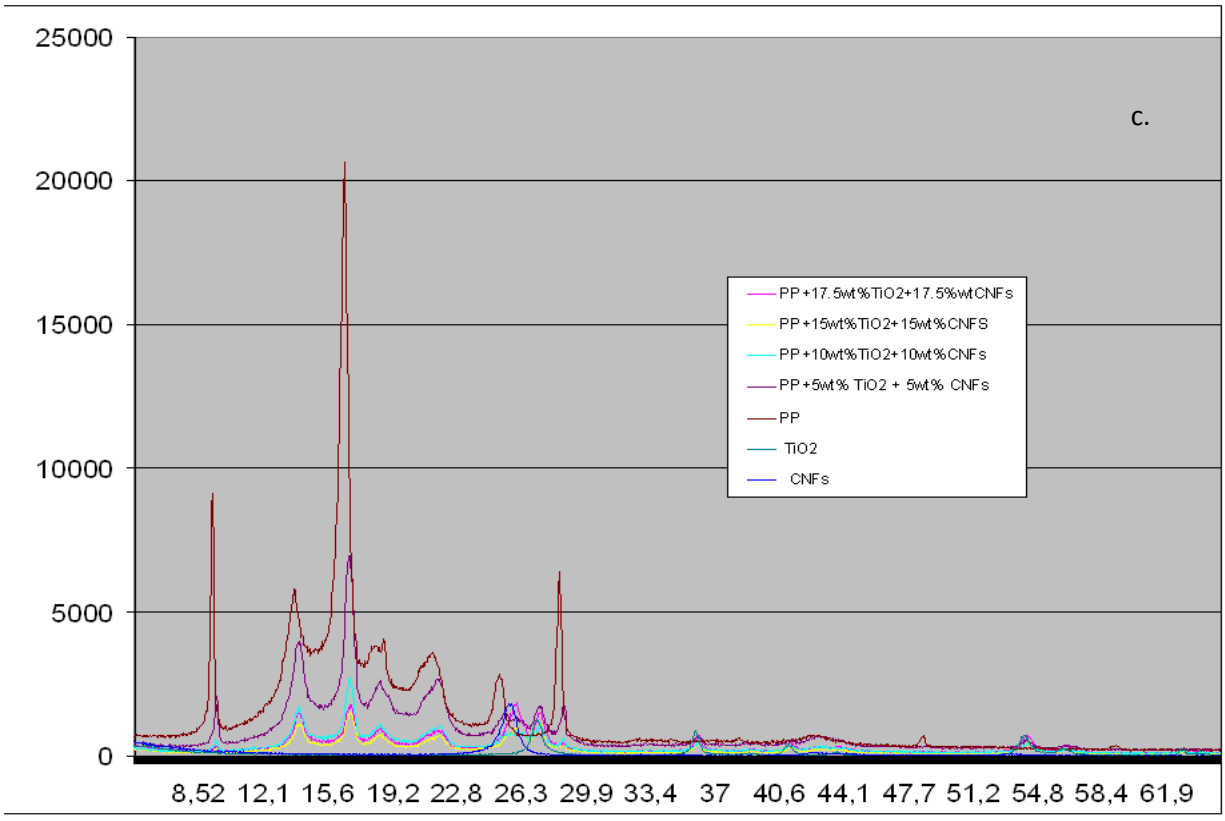


Fig.6-5 WXRD patterns of PP and CNFs filled PP(a.);TiO_2 filled PP(b.);CNFs/TiO_2 filled PP(c)

AFM

With regards to the investigation of the nano fillers dispersion in polymer matrix, the AFM measurement was applied as the characterization method. The nano fillers distributions on the surface of micro injection molded samples at a weight concentration of 10% were tested by AFM. From Fig.6-6, most nano fillers can be observed to disperse homogonously in the surface of the formed parts after micro injection molding, however, there are still agglomeration happened, especially for TiO2 nano particles, it is more obvious.

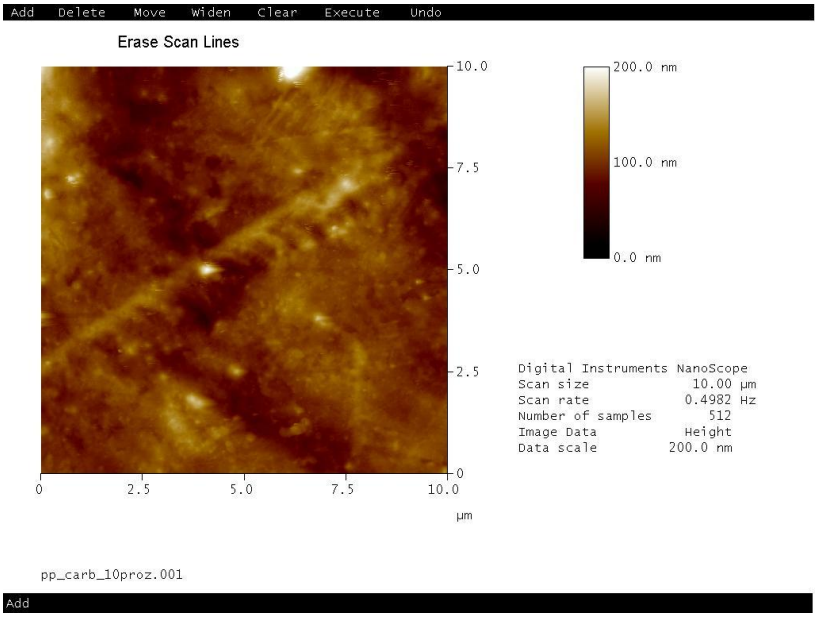


Fig.6-6a AFM measurement of PP+10wt% CNF

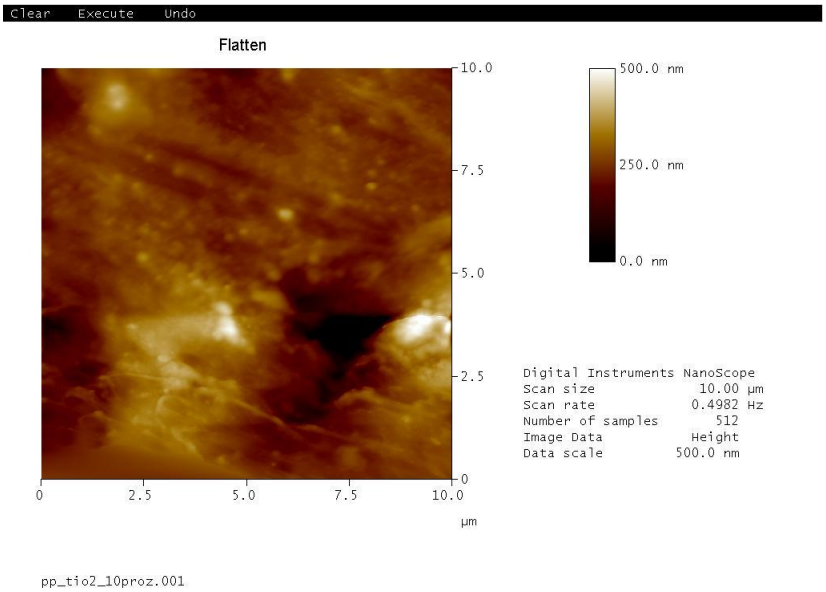
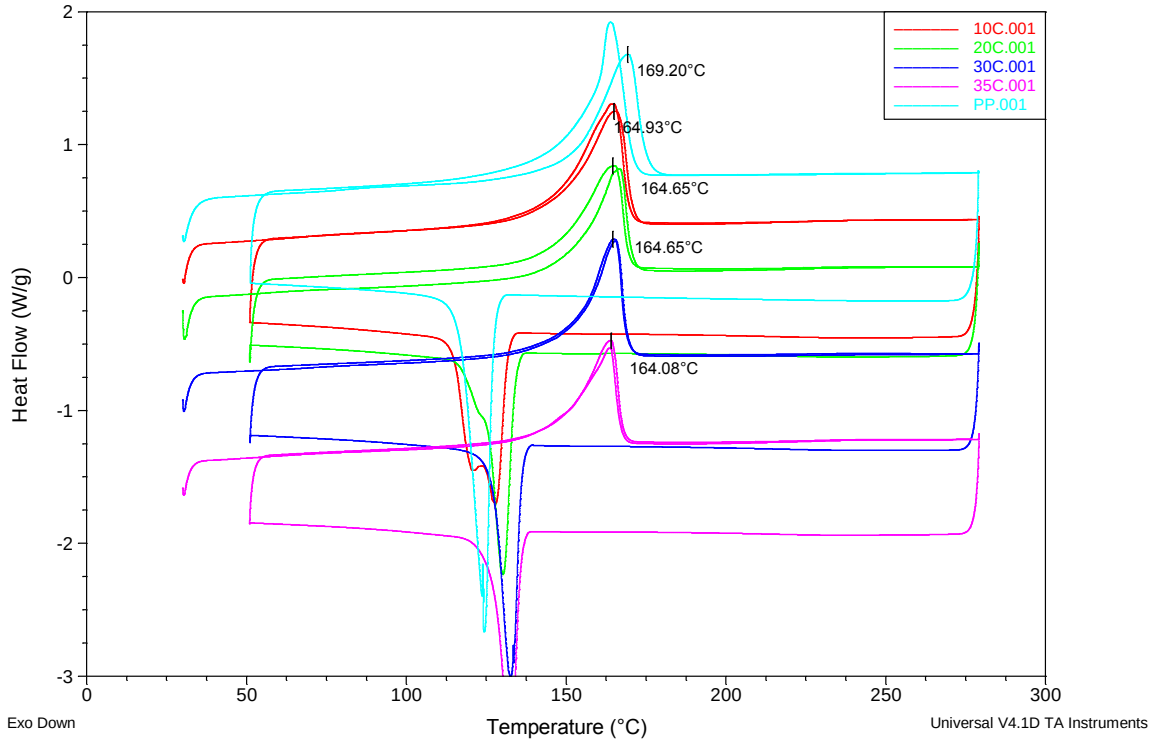


Fig.6-6b AFM measurement of PP+10wt% TiO2 nano particles

DSC

With DSC measurements, the heat flux versus time curve patterns for nano filled PP as well as unfilled PP were achieved, shown as in Fig.6-7. Based on those data, the peak temperature of crystallization melting (T_m) and the peak temperature of crystallization (T_p) were obtained and listed in Table 6-1. It implies that addition of nano fillers lead to higher peak temperature of crystallization melting (T_m) and increasing the loading levels above 10 wt% does not result in a further increment of T_m. The reason for this is that the polymer chains in nano filled PP composites are relative smaller than in pure PP because the nano fillers restrict the formation of a large polymer chain and make them smaller ones, which contributes to make the melting temperature of materials lower.

The peak temperature of crystallization of PP was increased due to adding nano fillers, which is the result from the action of nano fillers as nucleating agents for PP crystals. However, there is a limiting effect of nucleating crystallization happened when the loading content is higher than 30wt% for CNFs and 20 wt% for nano TiO_2. Based on the comparison of T_m between PP/CNFs composites and PP/TiO_2 composites, CNFs show stronger nucleating performance for promoting heterogeneous nucleation than TiO_2 nano particles. This result indicates that CNFs has better dispersion in PP matrix than TiO_2 nano particles, which is also supported by the XRD pattern analysis for the crystallite size of CNFs and TiO_2 in PP from previous part.



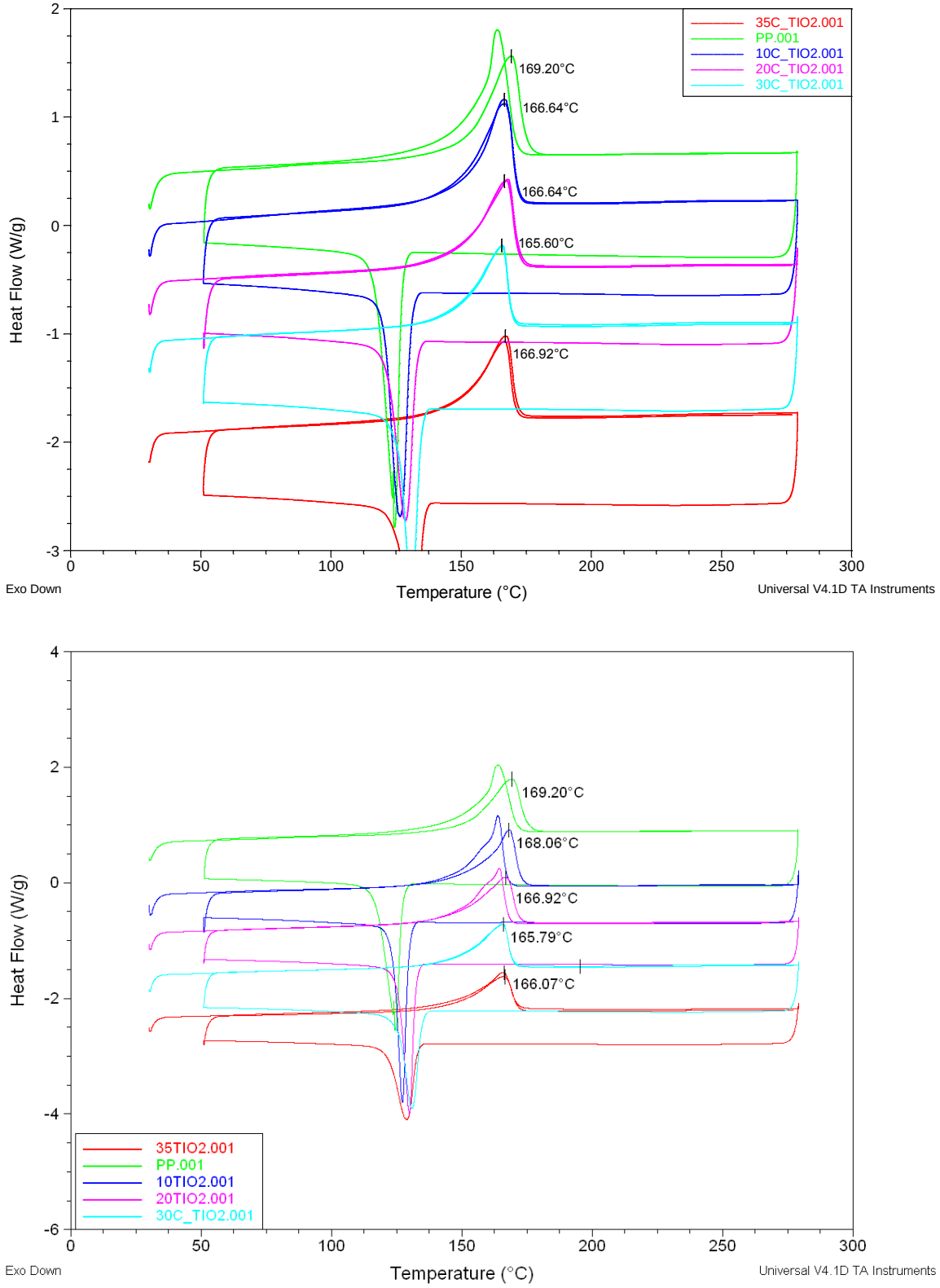


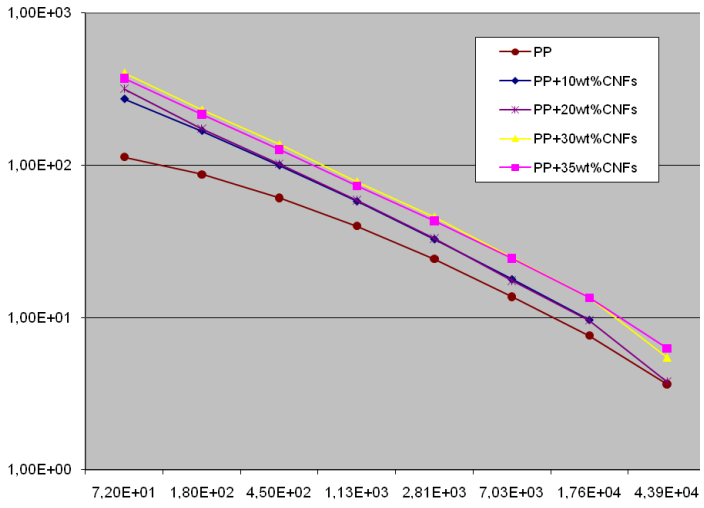
Fig. 6-7 DSC measuring curves for all nano filled PP composites

Table 6-1 Peak temperature of crystallization melting (T_m) and peak temperature of crystallization (T_p) of PP and nanofilled PP composites

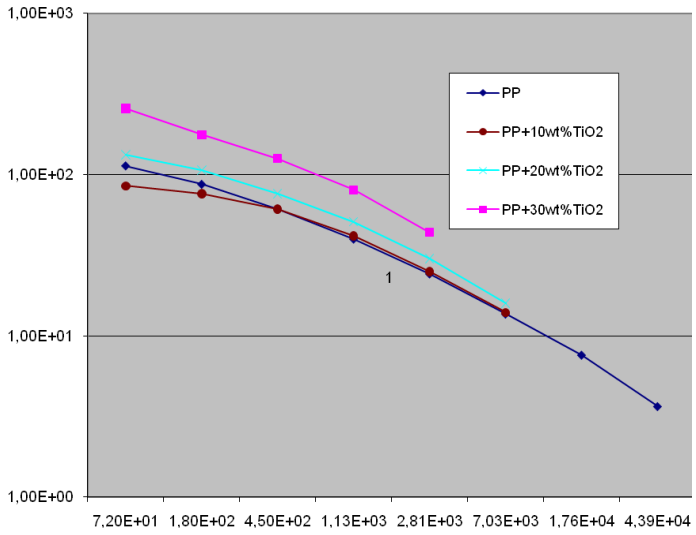
Materials	T_m(°C)	T_p(°C)
PP	169.20	124.28
PP+10 wt% CNFs	164.93	127.69
PP+20 wt% CNFs	164.65	129.96
PP+30 wt% CNFs	164.65	132.52
PP+35 wt% CNFs	164.08	132.52
PP+10 wt% TiO_2	166.64	127.40
PP+20 wt% TiO_2	165.60	129.68
PP+30 wt% TiO_2	165.60	129.39
PP+35 wt% TiO_2	166.90	129.11

Rheometer

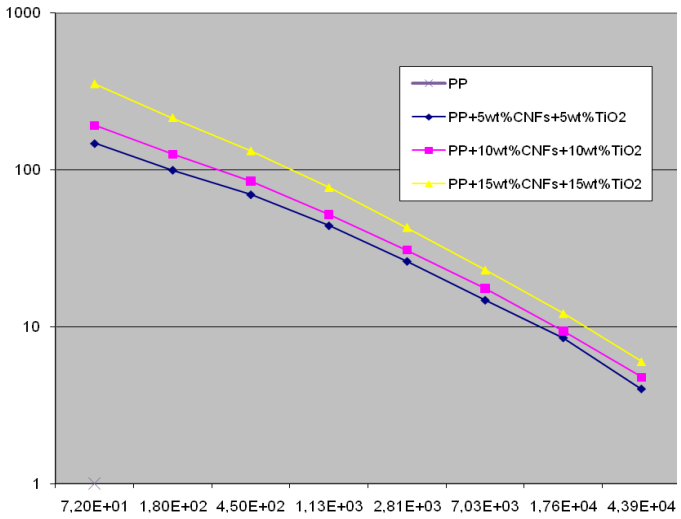
The viscosity – shear rate curves after Rabinowitsch correction obtained by high pressure capillary rheometer is displayed in Fig.6-8. From the results in Fig.6-8, it is clear that the viscosity of nano filled PP is generally higher than neat PP. Higher nano fillers loading fraction causes higher viscosity. At the same concentration, CNFs filled PP shows higher viscosity than TiO_2 filled PP, which is because CNFs bring more flowing restriction than TiO_2 nano particles attributed by the more intensive interaction of carbon nanofibers and nanofiblers - polymer chains.



a.



b.



c.

Fig.6-8 Viscoisty-shear rate curves for PP and nano filled PP composites:a.CNFs filled PP;b. TiO_2 filled PP; c. Hybrid CNFs/TiO_2 filled PP

6.2 Tensile test for weld line strength

Results

All the compounded nano composites were processed by Arburg® 220S injection molding machine to form the micro tensile samples with intended weld lines. Arburg® 220S is a micro injection molding machine, which has 15mm diameter screw, and can offer maxium 250 MPa injection pressure, 22 cm^3/s injection speed and 150 KN clamping force. The processing conditions during the micro weld lines tensile parts preparation are constant: melting temperature 230 °C, mold temperature 150 °C, injection pressure 100 MPa, injection speed 20 cm^3/s and ejection temperature 60 °C.

The tensile tests for molded weld line parts were implemented in the same procedure as Chapter 5 done. Mechanical properties of formed samples were mainly accessed by tensile test with the characterizations of tensile strength, E modulus and elongation at break. It should be mentioned that due to the extremely brittleness of samples made of 35wt% TiO_2/PP composites, there was no decent integrated samples able to be ejected during the micro injection molding process. Thus, the tensile test for this kind of composites was not implemented. The test results were plotted in Fig.6-9 till Fig.6-12.

Fig.6-9 shows the tensile strain-stress curves of neat PP and PP nano composites with various loading fractions. Due to the occurring of weld lines, there are no plasticity regions but elastic response regions for all tensile curves, which are similar to the results reported in the normal injection molding process [119]. The filling of nano fillers apparently aggravated the brittleness of micro tensile samples related to weld lines.

Fig.6-10a demonstrates that with the weld line presenting, micro tensile samples of CNF filled PP composites performed higher E modulus than the case of neat PP. The significant increase of the micro injection molded weld line can be observed when the CNFs were added into PP. With the increasing concentration of nano fibers, the responded E modulus of micro weld lines is increased. The increment of E modulus was not really marked from the comparison between 10 wt% and 20 wt% CNF concentrations. However, when the loading fraction of CNF is higher than 20 wt%, the impressive enhancement was exhibited. At 30 and 35 wt% of CNF, the increase in E modulus of 70% and 86% is presented respectively.

Whereas, compared with those of CNFs/PP composites, in Fig.6-10b. TiO_2 nano particles show different effects on micro weld line samples' E modulus. Weld line samples' E modulus are not increased but decreased due to the nano particles filling. However, with the increment of TiO_2 nano particle's concentration, the E modulus is getting higher after the fraction at 10 wt% and reaches the level higher than unfilled PP.

In Fig.6-10c, it can be found that by adding the hybrid nanofillers, the E modulus of weld lines of micro samples was improved. At a 10 wt% of CNFs/TiO2, the increment of E modulus of micro injection molded weld line is not evident; however when the content is higher than 20 wt%, E modulus is enhanced considerably, resulting 34% increase of E modulus at 35 wt% of CNFs/TiO2.

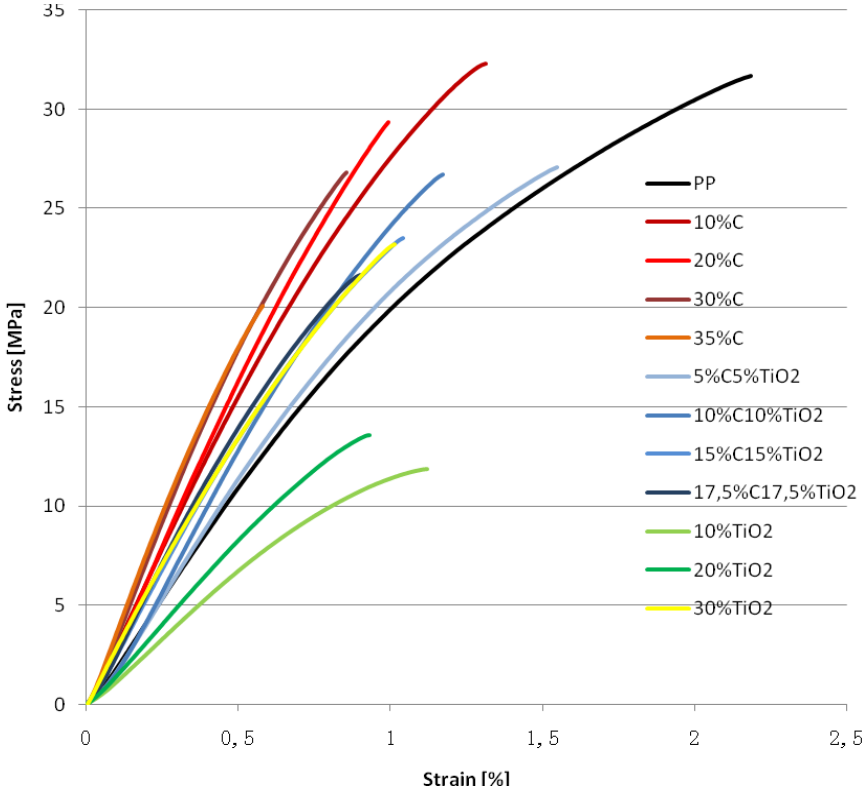
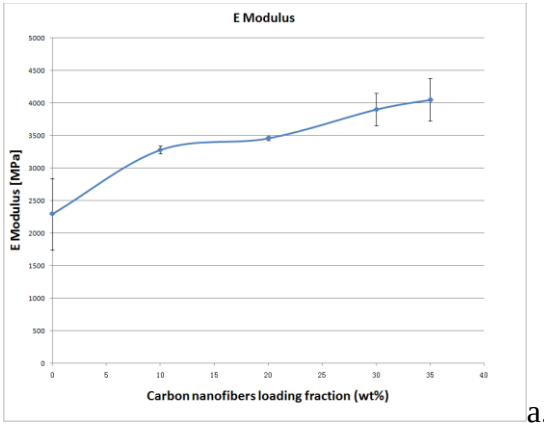
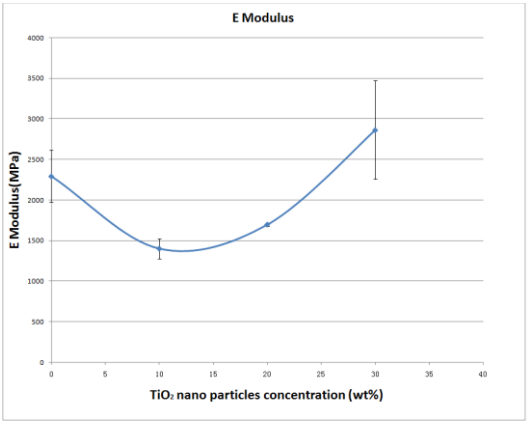


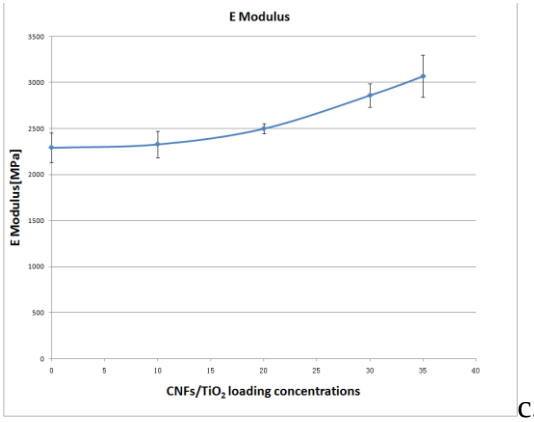
Fig.6-9 Tensile test strain-stress curve of mico weld lines samples with various nano filler concentrations



a.



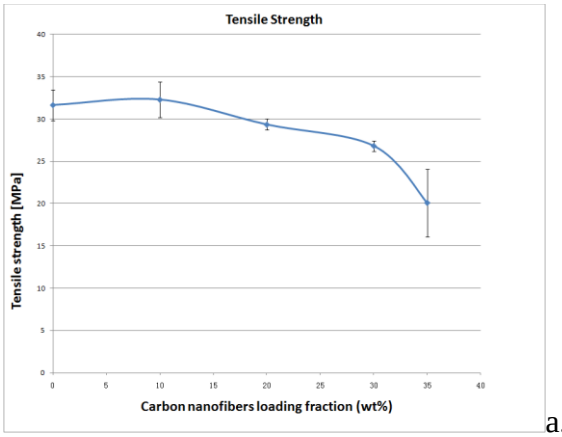
b.



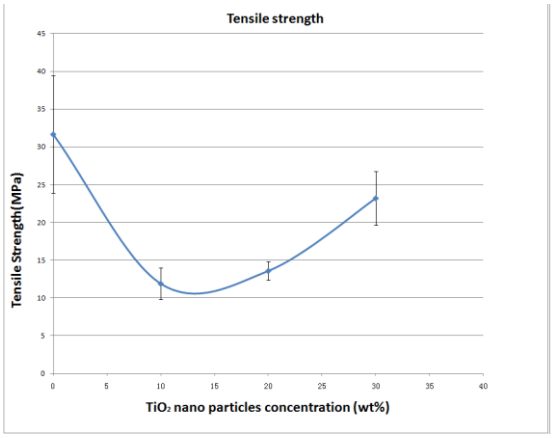
c.

Fig.6-10a E modulus of micro weld lines samples with various CNFs concentrations; Fig.6-10b E modulus of micro weld lines samples with various TiO_2 nano particles concentrations;Fig.6-10c E modulus of micro weld lines samples with various CNFs/TiO_2 concentrations

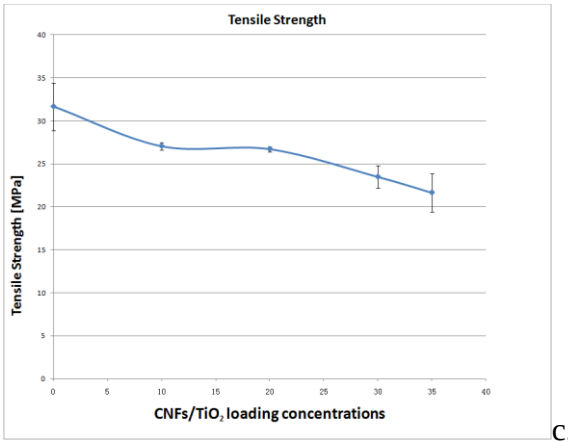
Tensile strength was named as the assessing characterization of the micro injection molded weld line strength, and the testing results were displayed in Fig.6-11, where it can be observed that with filling the CNF, tensile strength of samples was reduced in general than the case of pure PP, except for 10 wt% CNF/PP composites. Higher nanofibers contents lead to lower micro weld lines tensile strength. At 35 wt% CNF, the weld line strength was decreased dramatically compared to the other filling fractions. Regarding to TiO_2/PP nano composites, like the changing trend in correlation between E modulus and loading contents of TiO_2 particles, 10 wt% is also the critical content for tensile strength from decreasing trend to increasing. When the particle content rises to 30 wt%, the tensile strength is close to the value at 30 wt% of CNFs. As for hybrid CNF/TiO_2 filled PP, in Fig.6-11c., where the fact is able to be noted that generally filling hybrid nanofillers CNFs/TiO2 in PP is detrimental to tensile strength of micro injection molded weld line. Higher filling contents contribute to lower weld line strength. When the content is higher than 20 wt%, the weld line strength was reduced remarkably.



a.

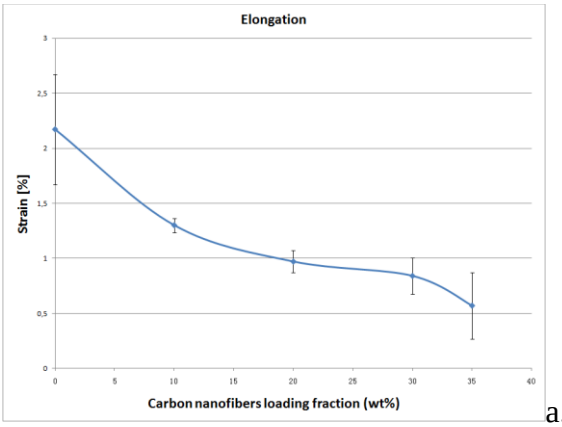


b.

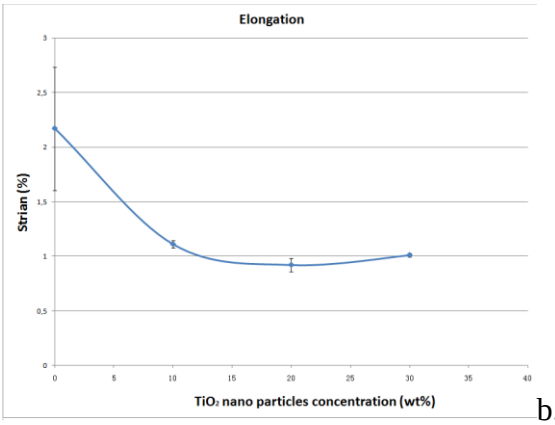


c.

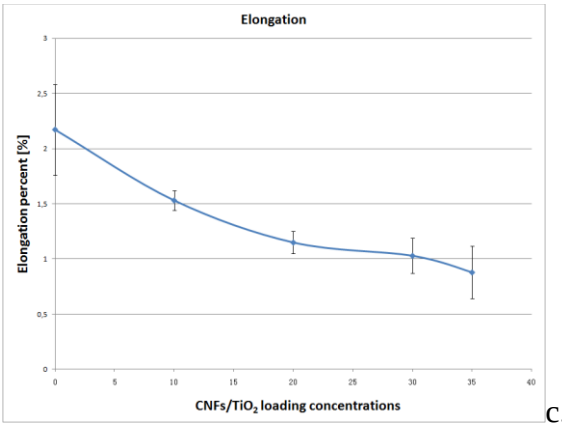
Fig.6-11a. Tensile strength of micro weld lines samples with various CNFs concentrations; Fig.6-11b. Tensile strength of micro weld lines samples with various TiO_2 nano particles concentrations; Fig.6-11c. Tensile strength of micro weld lines samples with various CNFs/TiO2 concentrations



a.



b.



c.

Fig. 6-12a. Elongation at break of micro weld lines samples with various CNFs concentrations; Fig.6-12b. Elongation percent of micro weld lines samples with various TiO_2 nano particles concentrations; Fig. 6-12c.

Fig.6-12 shows the correlation between the CNFs and TiO_2 nano particles loading fraction and the weld line tensile sample's elongation at break. Normally the tensile elongation of PP is relative high. With appearance of weld lines, the deformation percent will be radically decreased. In this study, the micro tensile sample with weld line made of unfilled PP showed 2.17%. With increasing CNFs content, the value of elongation for weld line samples was reduced more intensively, to 0.57% at a 35% of CNF content; as for TiO_2 nano particles, by 10 wt% filling of TiO_2, the elongation percent is decreased obviously, however as the filling fraction of TiO_2 increasing, the degree of decrement was not evident changed, the elongation percent was 1.11% at 10 wt% loading of TiO_2 and 1.01% at 30 wt% loading of TiO_2. With increasing CNFs/TiO2 fractions, the value of elongation for weld line samples was dramatically decreased, to 0.88% at a 35wt% of CNFs/TiO2.

Analysis and Discuss

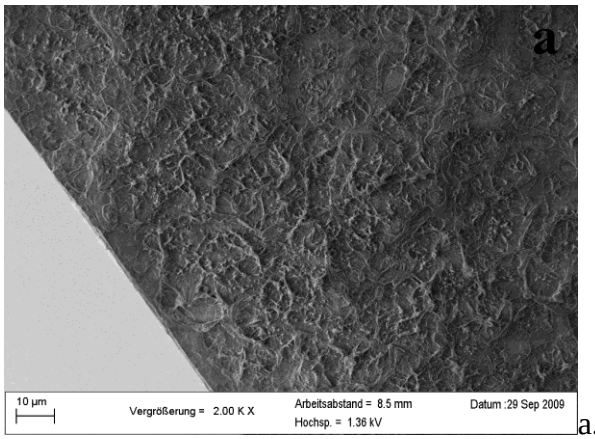
Effect of CNFS

As very well known, except for low or ultra low wt% (<1 wt%), the tensile ductility of polymer matrix is deteriorate considerably by adding CNFs, which can be the results from modifications in the crystalline fraction of the polymer matrix or increasing agglomeration of CNFs within polymer matrix[120-122]. The fact of improved E modulus and reduced elongation of micro weld line tensile samples suggests that there are the same effects of CNFs on micro weld lines ductility as the case without it. Additionally, the more isotropic complex

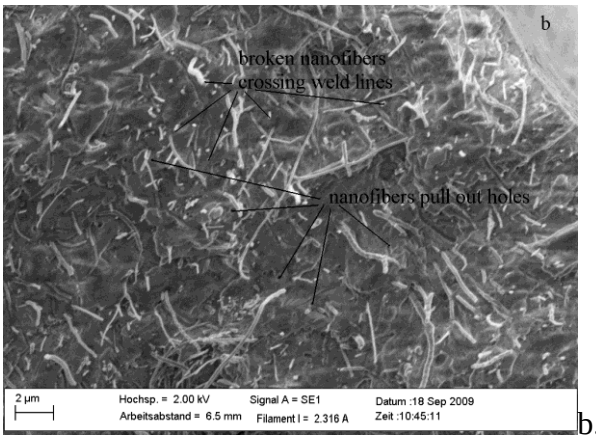
distribution and orientation of nano fibers in weld line areas contribute to more restriction sites preventing the polymer from deformation, therefore resulting in a decrease in ductility and an increase in brittleness of micro injected weld lines with PP/CNFs.

The decreased tensile strength of micro weld lines by loading CNFs could be caused by the nano fillers aligning perpendicular to the flow direction at the weld line and their non-uniform distribution, which is similar as the results reported in conventional injection molded weld line study [119]. Additionally, the planar orientation of nano fillers may also hinder molecular chain motion on solidification and inhibit optimal crystalline development and orientation in the weld line region.

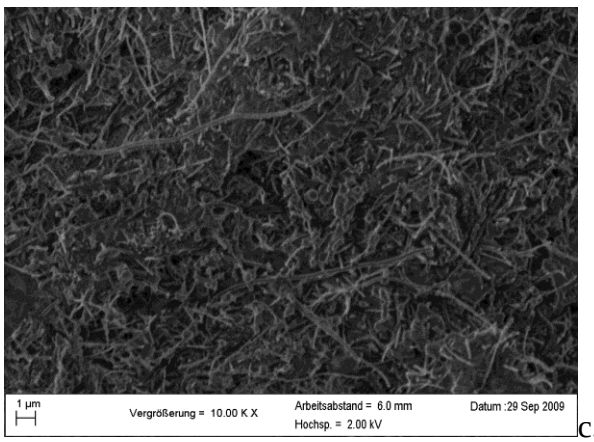
As the nano fibers content increasing, the fiber's perpendicular orientation to the overall melt flow direction at weld line plane will be more, hence more polymer chains are induced to orient in the same way. Then when both the flow fronts impinge at the weld line, the nanofibers and polymer chains together orient perpendicular to the flow direction, which will make a weld lines with lower strength, hence the 35wt% case showed the worst weld line strength. In Fig.6-13, it is obviously illustrated and visible that when carbon nanofibers weight content is higher than 20 %, there are many orientations of nano carbon fibers perpendicular to flow direction in weld line areas, and their footprints were evident.



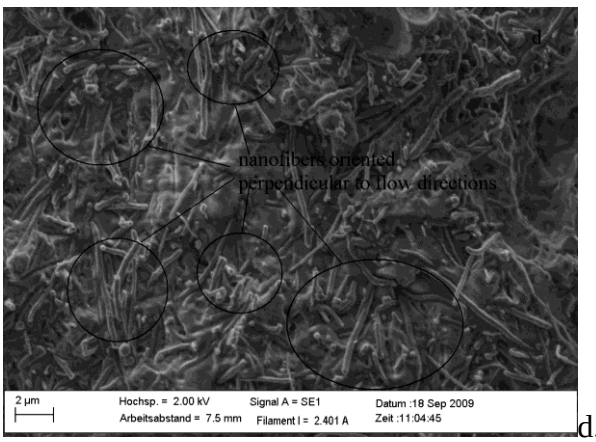
a.



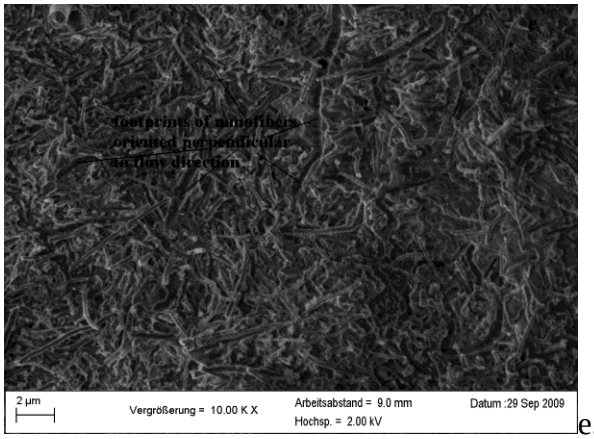
b.



c.



d.



e.

Fig.6-13 SEM images of weld line samples tensile test broken section for various wt% CNFs filled composites: a. neat PP; b. PP+10%Carbon nano fibers; c. PP+ 20% Carbon nano fibers; d. PP+30% Carbon nano fibers; e.PP+35% Carbon nano fibers.

As for 10% CNF/PP composites system shows a relative higher tensile strength than neat PP, it is because when the fiber filling grade is low, at the weld line a small amount of nano fibers may align parallel to flow direction and across the weld line due to the relative higher shear rate in micro injection molding process, which will work as an enhancement for weld lines' tensile strength. Fig.6-13b shows at 10 wt% of nano fibers, pull out holes and broken marks of nano fibers crossing weld lines are distributed widely in the weld line broken sections.

Effect of TiO_2 nano partiles

For the phenomena of unexpected decreased E modulus at 10 and 20wt% of TiO_2 filling in PP, the reason could be that at relative lower concentration the agglomeration of TiO_2 nano particles reduced the theoretical performance of nano particle in enhancing polymer matrix stiffness which is predicted by Halpin-Tsai theory under perfect dispersion assumption[26]. However, with the filler contents increasing, the agglomeration of particles is relatively limited increased, thus there are more chances for nano particles to be well dispersed in matrix and induce the occurrence of polymer chains intercalations which will improve the stiffness even there are still agglomeration existing. The SEM images in Fig6-14 clearly show the distribution situation of particles at 10wt% and 30wt% of TiO_2 nano particles, which can support the explanation above.

Same as CNFs/PP composites, the tensile strength of TiO_2/PP composites is lower than that of unfilled PP, which is also because the more direct interconnections among nano particles in weld line areas. And like the effect on E modulus, the changing situation of nano particles agglomeration with the increment of TiO_2 loading also lead to the increase of tensile strength of micro weld line sample at 30 wt% loading of TiO_2.

In general, the ductility of micro weld line samples was decreased by adding nano particle of TiO_2, but the stiffness was increased at high loading fraction (30wt%).

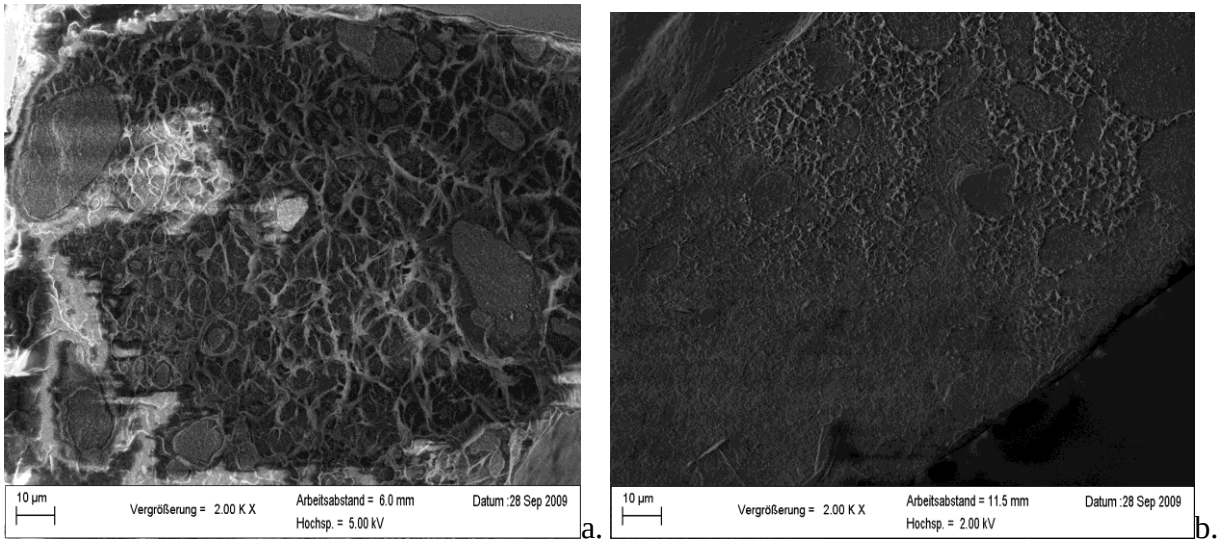
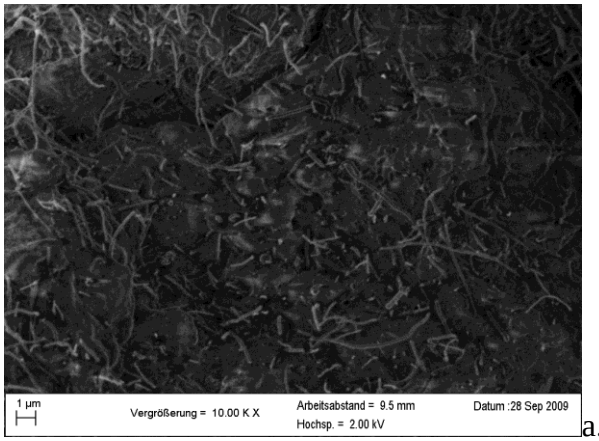


Fig.6-14 SEM morphology of PP/TiO_2 nano composites with different loading contents: a.10wt%; b.30wt%

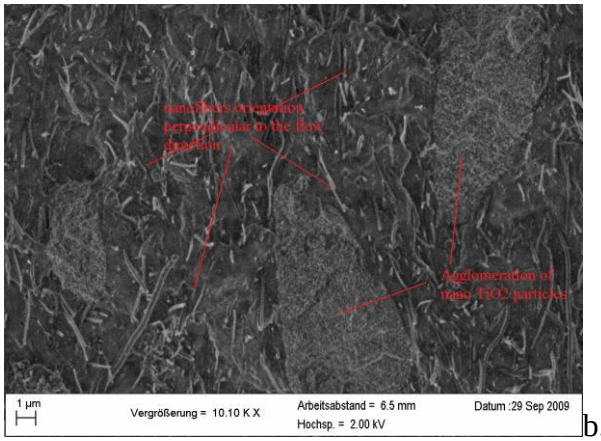
Effect of Hybrid CNFS/TiO_2 nano particles

As for hybrid CNFs/TiO2 reinforced PP, the increase in brittleness of micro injection molded weld lines is also clearly able to be observed comparing with unfilled PP. The possible explanations for this are same as those of CNFs and TiO_2 above mentioned that the orientation of CNFs perpendicular to flow direction in the weld line section restricts the entanglement of polymer chains in this welding area; additionally interaction and agglomeration among TiO2 nano particles in weld line area reduces this entanglement of polymer chains as well. Furthermore, this reduction in tensile ductility is considered to be associated with changes that occurred in the crystalline fraction and state of PP matrix where the crystalline degree and spherulite size were altered.

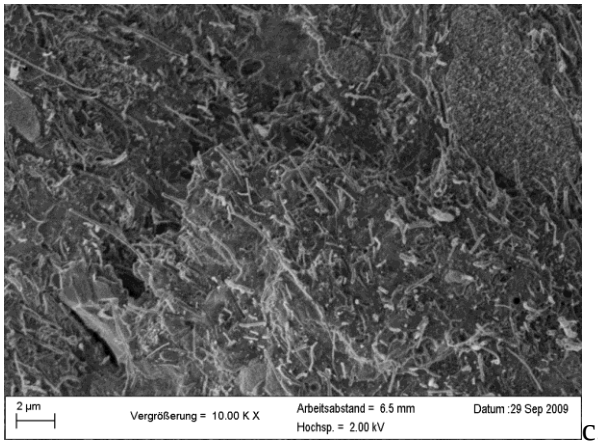
Fig.6-15 shows the scanning electron micro graphs on tensile broken sections of micro injection molded weld line with various hybrid CNFs/TiO2 concentrations. The nanofibers' perpendicular orientation to flow directions and the exposed nano particles' agglomeration in weld line sections are enable to be clearly seen.



a.



b.



c.

Fig.6-15 SEM images of weld line samples' tensile test broken sections for various wt% CNFs/TiO_2 filled composites: a. PP+ 10wt% CNFs/TiO_2; b. PP+ 20wt% CNFs/TiO_2; c. PP+30wt% CNFs/TiO_2.

Weld line strength modeling

We assume that the micro injection molded weld line strength with nano filled PP is a function of nano filler's concentration and their distribution only. Based on the tensile test results in this study, a second order polynomial weld line predicting equation was obtained by Newtonian iteration fitting method, shown as Equation (6-1).

$$\delta_w = a_1 \varphi^3 + a_2\varphi^2 + a_3\varphi + \delta_m \quad (6\text{-}1)$$

Where, δ_w is weld line strength, φ is nano fillers concentration, a_1, a_2 and a_3 are constant coefficients related to the filler features (filler's aspect ratio, dispersion situation etc.), δ_m is tensile strength of polymer matrix. This empirical equation is supposed to predict the micro weld line strength in case of higher nano filler contents than 10 wt%, since in lower content (<1wt%) the influence of nano fillers is conversely different according to reported literatures[120]. The corresponding trend fitting lines of the tensile strength of weld lines for various nano filled composites based on Equation (6-1) are plotted in Fig.6-16.

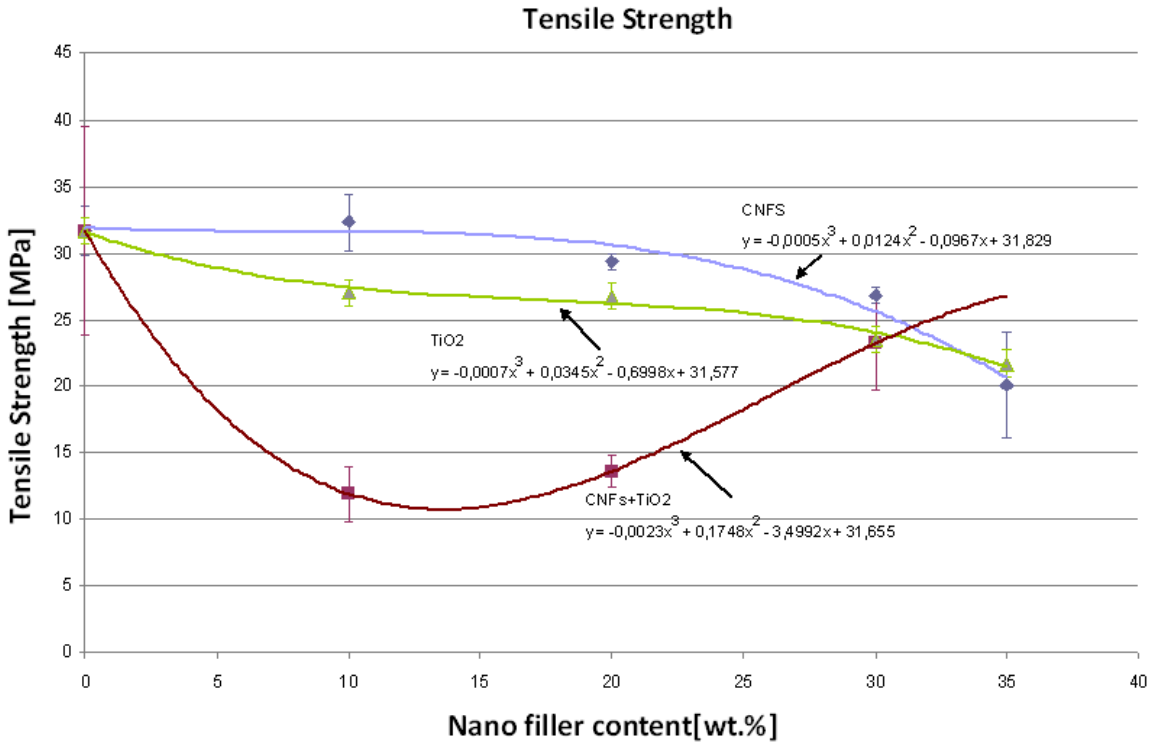


Fig.6-16 The fitting trend line for micro injection molded weld line strength based on the empirical prediction equation

Summary

According to the results gained above, some conclusions can be drawn:

1. The PP/nano composites were prepared by a low shear twin screw kneader, and the filler distribution in polymer matrix was characterized by AFM, XRD and SEM; The thermal and rheological properties were measured also; By tensile testing, it was found the loaded nano filler influenced the micro injection molded weld line strength of PP dramatically;

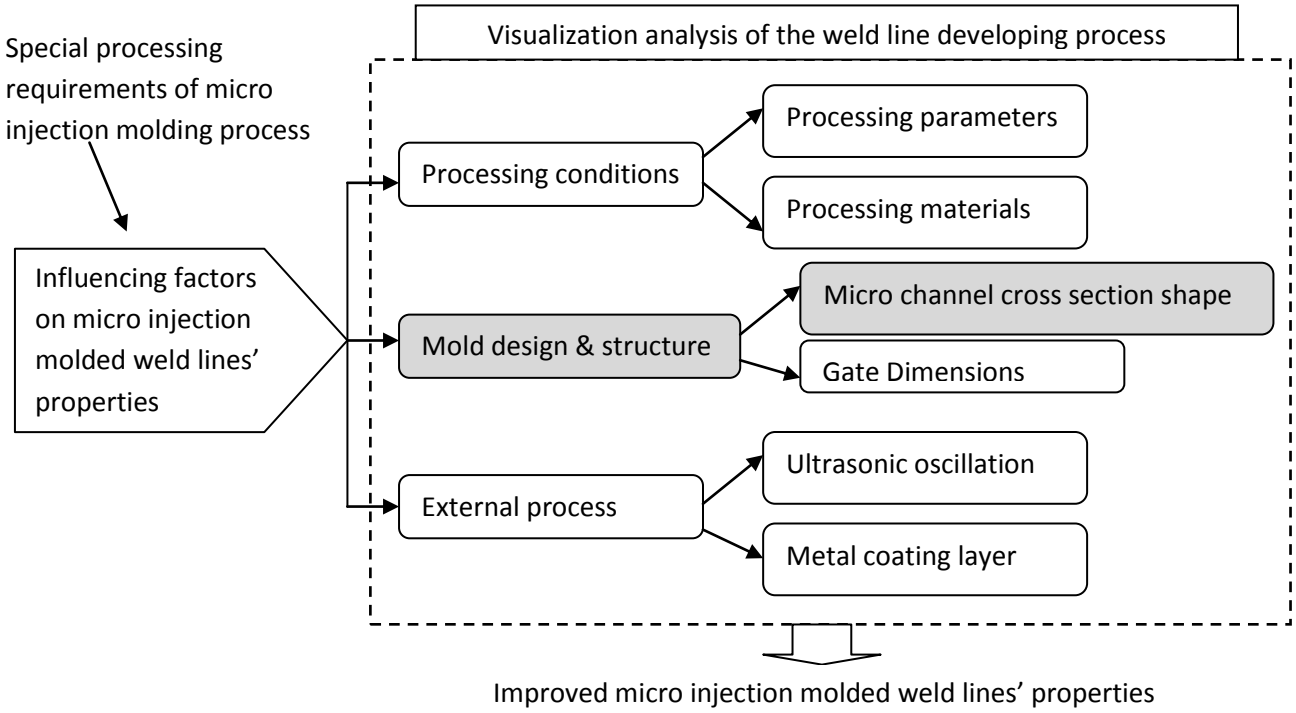
2. The micro injection molded weld lines of CNF filled PP and hybrid CNF/TiO_2 filled PP have higher E module than neat. And with the concentration increasing, the E module is also increased. For TiO_2 nano particle filled PP, the weld line samples' E module are not improved but decreased. However, with the increment of TiO_2 nano particle's concentration, the E module is getting higher after the threshold fraction 10 weight% and reaches the same level as hybrid CNF/TiO_2 filled PP at 30 weight%;

3. In the study, almost nano composites are having lower tensile strength than neat PP, besides the case of 10 weight% CNF. For CNF and hybrid CNF/TiO_2 composites, higher filler contents lead to lower tensile strength, excluded 10 weight% CNF/PP; for TiO_2 nano composites, 10 weight% is the critical content for the relation of tensile

strength from decreasing trend to increasing. When the particle content rises to 30 weight%, the tensile strength is equal to the hybrid CNF/TiO_2 composites.

4. The weld line area's strain-to-failure of all nano composites are lower than neat PP. When the nano fillers' weight loading is lower than 20%, the weld line of nano CNF and hybrid nano CNF/TiO_2 composites correspond to larger tensile strain than nano TiO_2 composites; When higher than 20%, the weld line of nano TiO_2/PP system demonstrates the higher strain-to-failure value.

5. Finally, an empirical prediction equation for micro injection molded weld line strength of nano PP composites was proposed for higher nano filler loading fraction than 10 wt %.



Mould Design and Structure Factor I

7 Effects of micro channel cross section geometry and dimension on weld line strength

In injection molding process, the channels and cavities' geometry structure and dimension have significant impact on the melts flowing and filling behavior, which influence the mechanical properties of the final molded parts. Nevertheless, the investigation and attention on the correlation between the mould structure and weld line mechanical properties are pretty limited in micro injection molding field. In the presented chapter, an experimental study on correlation between cross section shape and micro injection molding weld line strength was actualized in different injection pressures, injection speeds, melt temperatures and mold

temperatures in order to systemically obtain the correlation between micro channel cross section shapes and micro weld line strength.

7.1 Experimental principle and setup

7.1.1 Principle

A micro injection mold with multi cavities of micro tensile bar was designed and constructed. These micro cavities are fabricated by a micro milling process in different cross section shapes and dimensions (semicircle, equilateral triangle and trapezoid). With the injection molding machine, micro tensile test sample are prepared in different processing parameters so that a correlation between the cross section shapes with micro weld line strength in different conditions could be investigated by tensile test.

7.1.2 Injection mould design and manufacture

The micro cavities used in experimental mold are fabricated by ultra high speed micro milling machine, Kugel GMbH, maxim speed 160,000 rpm with 5 axis freedoms, presented in Fig.7-1. In order to get different cross section shape, the micro milling cutters with relative profiles were also prepared. The roughness of final micro cavities' surfaces was not perfect mirror appearance, but it won't affect the experimental results related to micro injection molded weld lines, since the magnitude of the micro channel is much larger than the surface roughness here.

These cavities which have different cross section shapes (semicircle, equilateral triangle and trapezoid) are machined in one brass insert, shown in Fig.7-2.

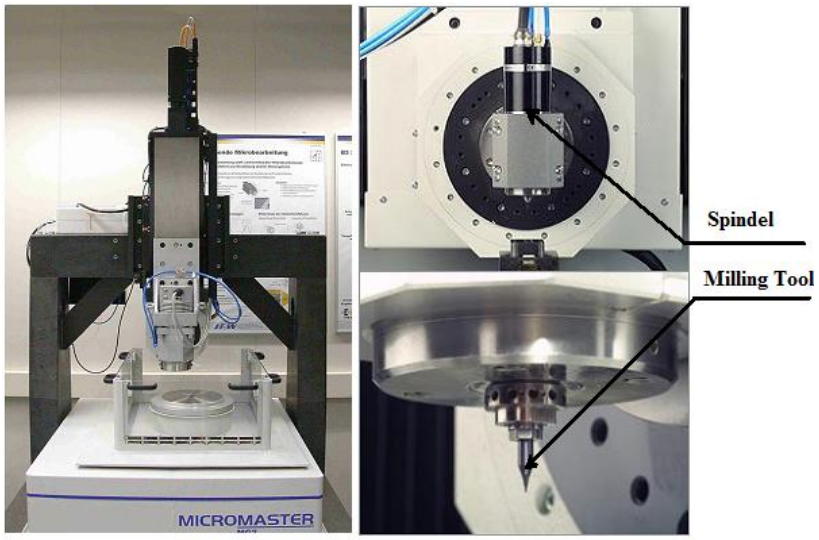


Fig.7-1 High speed micro milling machine with 5 axis freedoms

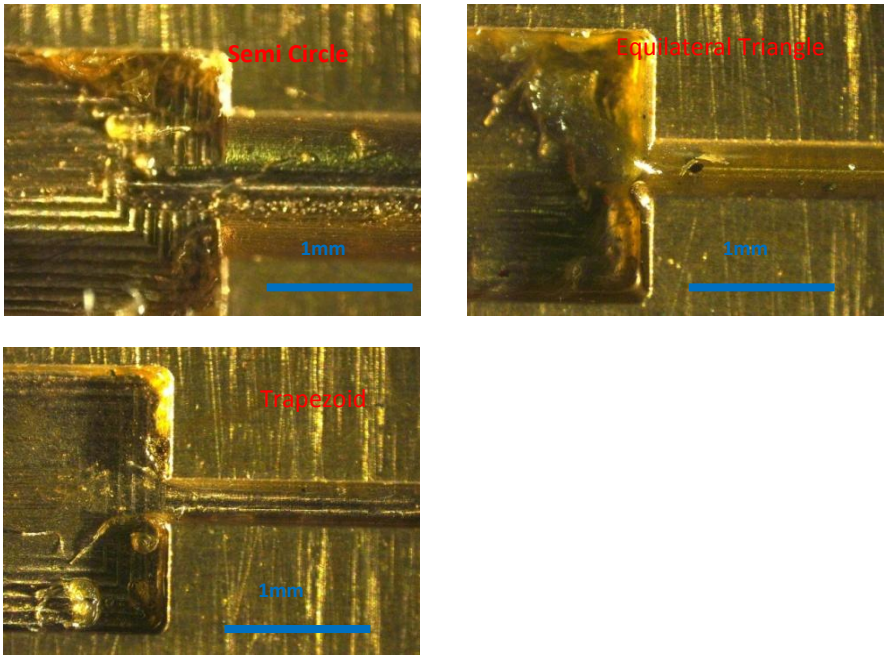


Fig.7-2 the Micro cavities with different cross section shape observed with microscope

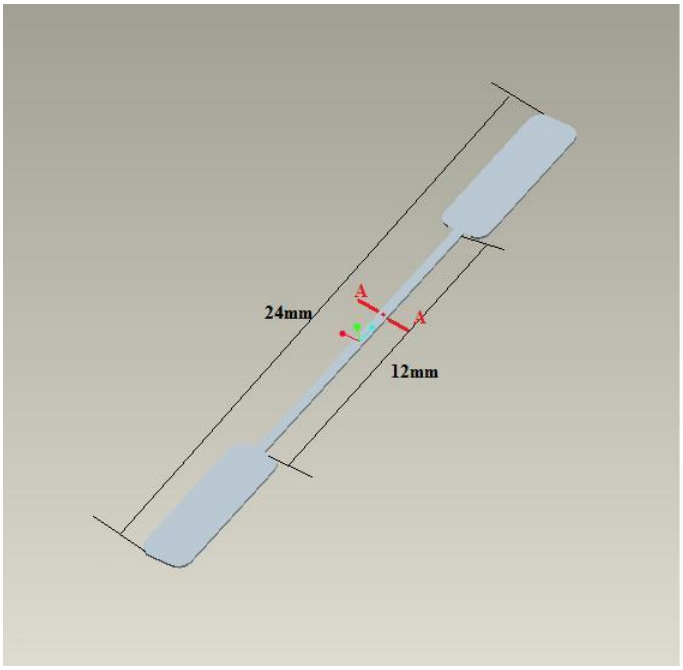
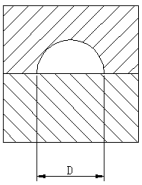
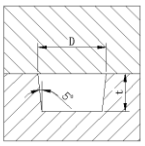


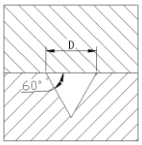
Fig.7-3a. Specimen geometry and dimension



D=1 mm



D=0.336mm, t= $\frac{2}{3}$ D



D=0.3mm

Fig.7-3b. Geometry and dimensions of the different cross section shapes for micro tensile sample

The whole lengths of all three micro tensile specimens are constant 24mm and the length of test area is 12mm, but three of them are different in A-A cross section shape, shown as Fig.7-3a. The dimensions and geometry of the micro tensile specimen A-A cross sections are displayed in Fig.7-3b.

For the sake of controlling the mold temperature with rapid conresponses, a variotherm unit was also integrated in the mold whose structure is similar to the mould used in Chapter 5, comprising of 6 electrical heating elements used as the heating part and cooling channels with the cold water at 18 ºC used as the cooling media.

7.1.3 Strategic experimental progress

To investigate how the cross section shape affects the weld line strength in micro injection molding in different processing conditions (melt temperature, mold temperature and injection pressure), an experimental plan was set up and performed, shown in Tab.1. Injection speed is fixed in 112cm^3/s and holding pressure is always set as 80% of injection pressure.

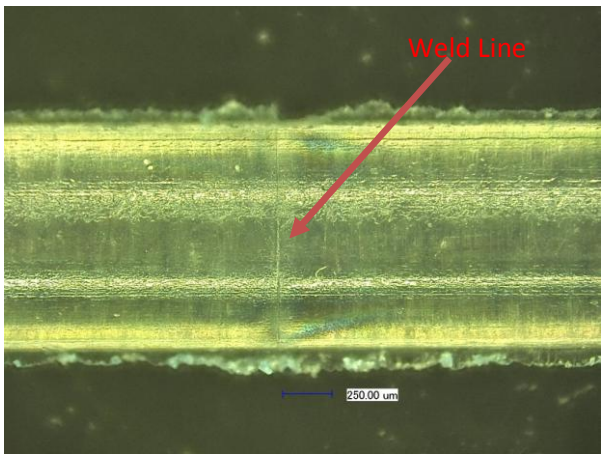
Table 7-1 Experiments performed in different processing parameters

Experimental Nr.	Melt temperature(ºC)	Mold temperature(ºC)	Injection pressure (MPa)
1	240	120	100
2	240	120	150
3	240	130	150
4	240	130	180
5	260	130	180

After injection molding experiments, the molded micro samples with weld lines were applied to tensile tests and determine the weld strength variation in different cross section shapes and processing parameters.

7.2 Correlation between cross section shape and weld line mechanical properties coupling with processing parameters

Following the experimental plan list in Table 7-1, the micro tensile parts are prepared and Fig.7-4 shows the samples formed by micro injection molding and the weld lines in the middle of them. From the figures, the flashes are observed due to the unsealed gap between moving and fix parts of mould, whose depth are less than 0.001 mm. This depth could be believed not to influence the real strength of micro weld line.



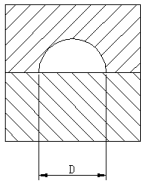
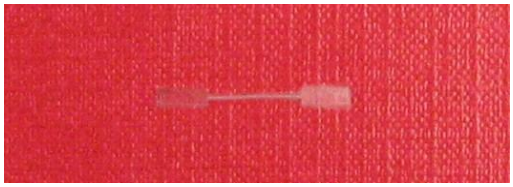
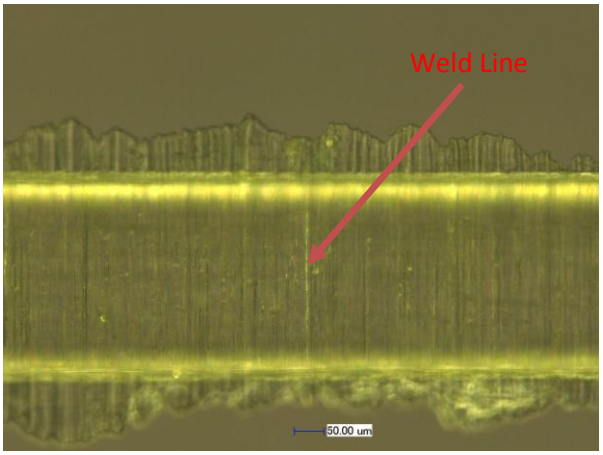


Fig.7-4a. Micro tensile specimen with Semi circle cross section and its weld line





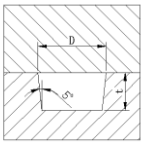
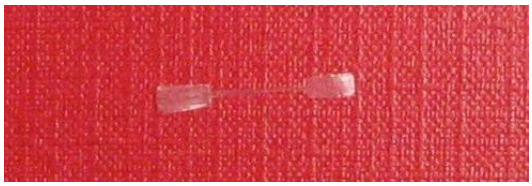
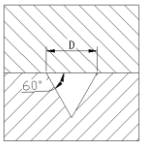


Fig.7-4b. Micro tensile specimen with trapezoid cross section and its weld line





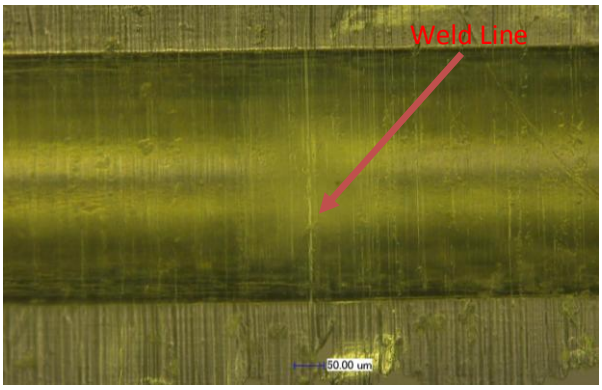
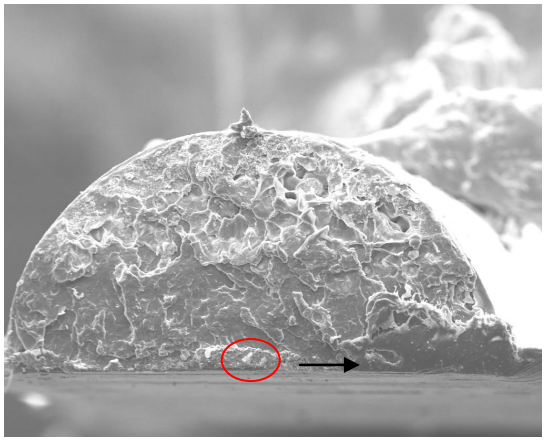


Fig.7-4c. Micro tensile specimen with equilateral triangle and its weld line

After tensile test, the broken sections for these 3 cross section shape samples were observed under scan electronic microscope (SEM), presented in Fig.7-5. The pictures show out the broken cross section area of semicircle cross section tensile sample is mainly portion of brittle broken appearance, which is means the polymer molecular entangled each other not very well, and will lead to worse tensile strength. The situations of the other two kinds of cross section tensile samples are different. Their broken features are mainly elastic broken, especially for tensile sample with equilateral triangle cross section shape, there are only thin skin layers and core entangled polymer occupied the main cross section area, which are obviously able to be observed from magnified pictures in the angles of broken area (Fig.7-5c). The profiles of the parts are also illustrated in the pictures. The replicated quality of semi circle tensile sample with relative large dimension (Ratius is 0.5mm) is the best.



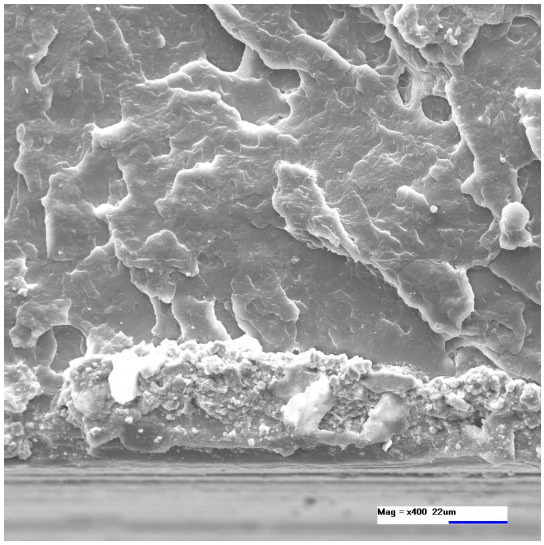


Fig.7-5a Semi circle micro tensile sample broken section

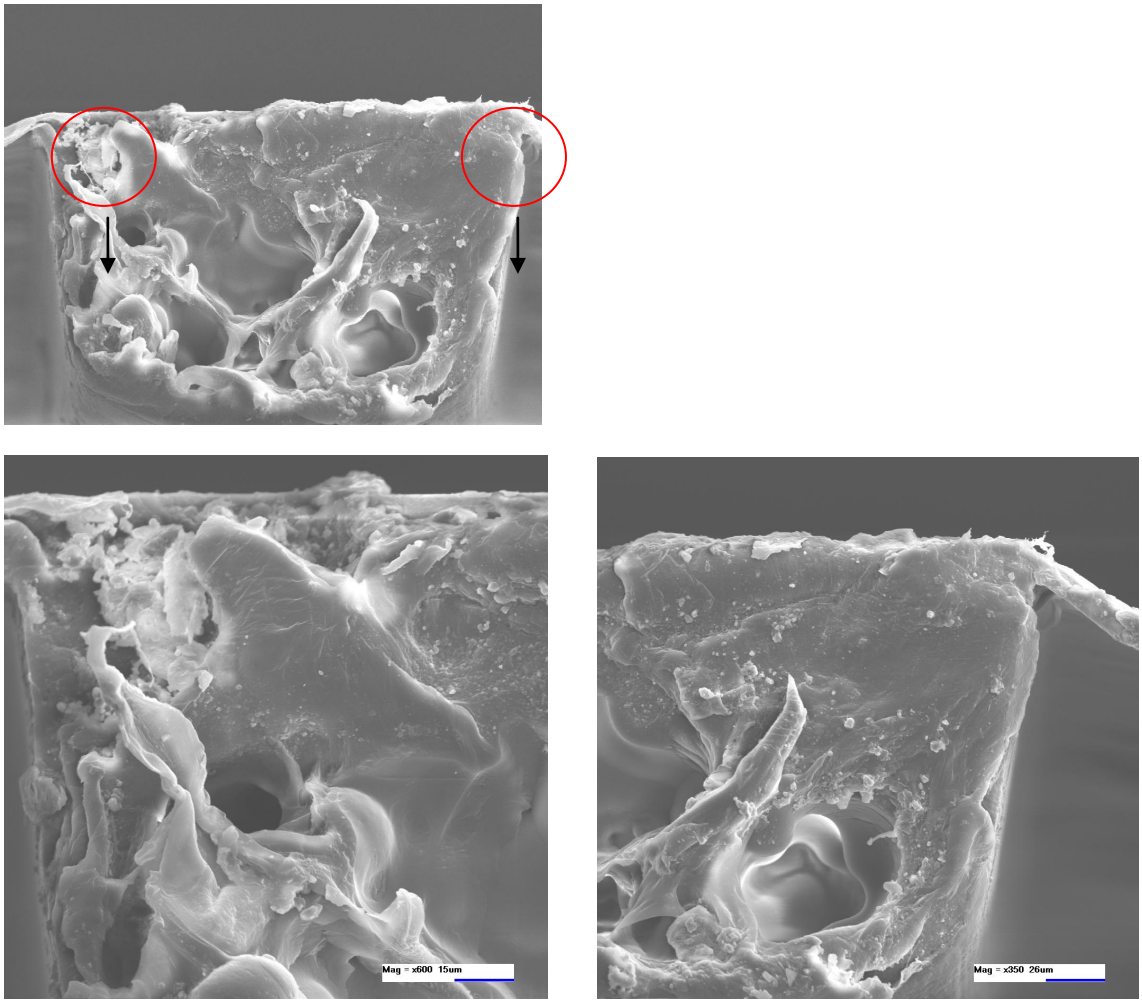
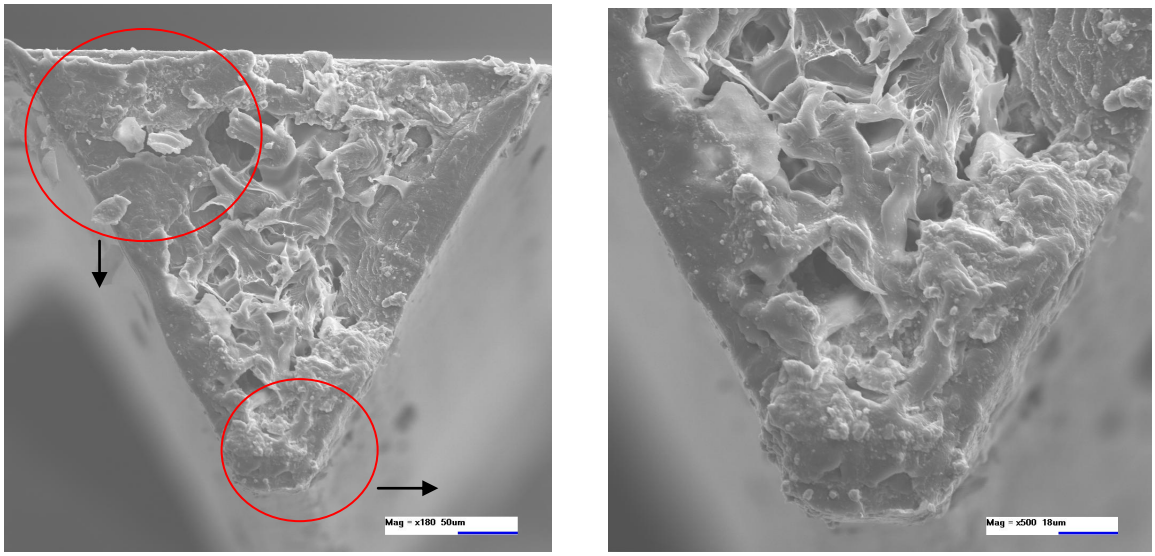


Fig.7-5b Trapezoid micro tensile broken section



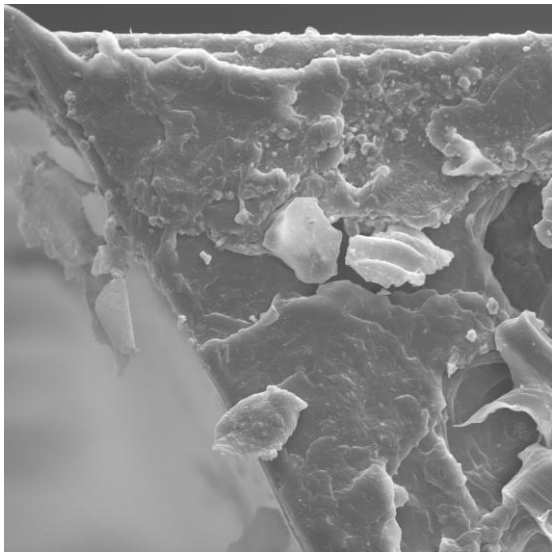


Fig.7-5c Equilateral Triangle micro tensile broken section

In order to proof the precision of the test research, every experiment was repeated 5 times and tested for ultimate breaking strength of micro weld line, the average values of test results are plot in Fig.7-6 till Fig.7-8. From Fig.7-6 and 7-7, one can find that for all cross section shapes, higher injection pressure induced lower weld line strength whatever the mold temperature is 120 ºC or 130 ºC. According to Fig.7-7, there is the fact showing that only for equilateral triangle cross section, higher mold temperature leads to higher weld line strength, while for other cross section shapes, mold temperature does not show an obvious effect on weld line strength. Fig.7-8 reveals the same influencing relation of melt temperature to weld line strength as mold temperature shown.

Nevertheless, whatever processing parameters variing, the relation between cross section shape and weld line strength is always same. Equilateral triangle cross section contributes to strongest weld line, and then followed by trapezoid, semi-circle is the last.

In the aim to describe the cross section shape by a quantitative factor, a factor defined by the ratio of cross section perimeter to area was set up, which is shown as the following equation (7-1):

$$a = \frac{L}{S} \tag{7-1}$$

Where a is the quantitative factor, L is the perimeter of the cross section, and S is the area of the cross section. When a is higher, it means per unit area, the corresponding cross section shape will contribute to longer encountering weld line, which could relate to stronger weld line strength.

By the dimension of the different cross section listed in Fig.4, the value of *a* factor for semi circle, equilateral triangle and trapezoid used in this study were calculated respectively, presented in Table 7-2.

Table 7-2 Value of *a* factor for the applied different cross section shape in this study

	Semi circle	Equilateral triangle	Trapezoid
a factor	6.55	23.08	16.04

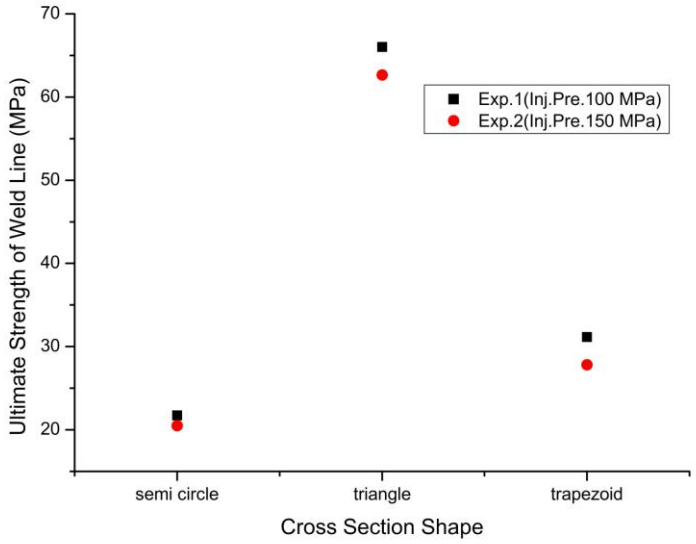


Fig.7-6 Weld line strength corresponded to different cross section shape in different injection pressure

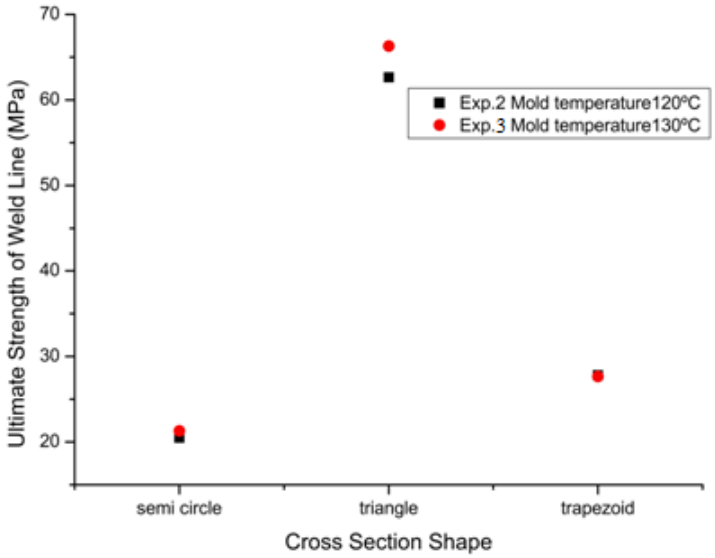


Fig.7-7 Weld line strength corresponded to different cross section shape in different mold temperature

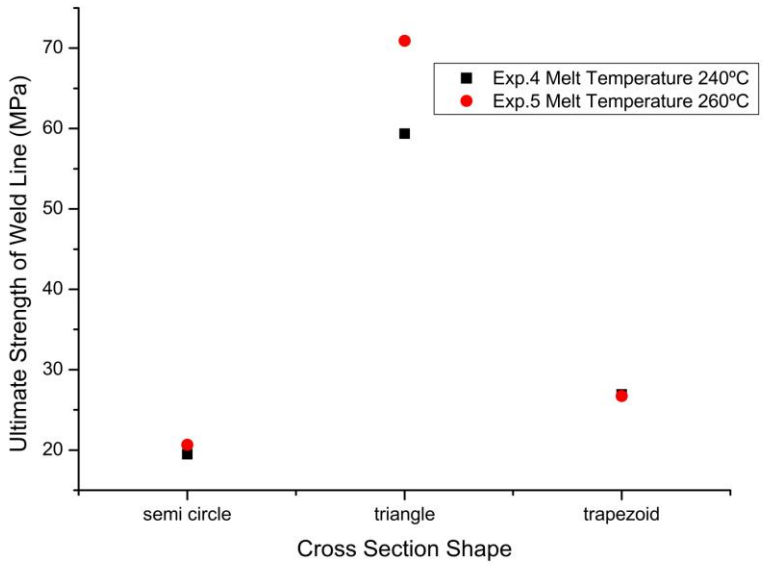


Fig.7-8 Weld line strength corresponded to different cross section shape in different melt temperature

This is consistent to the tensile test results shown in Fig.7-6 till Fig.7-8. Equilateral triangle cross section with higher *a* factor responses to higher ultimate breaking strength of weld line, followed by trapezoid and semi circle cross section in sequence.

Summary

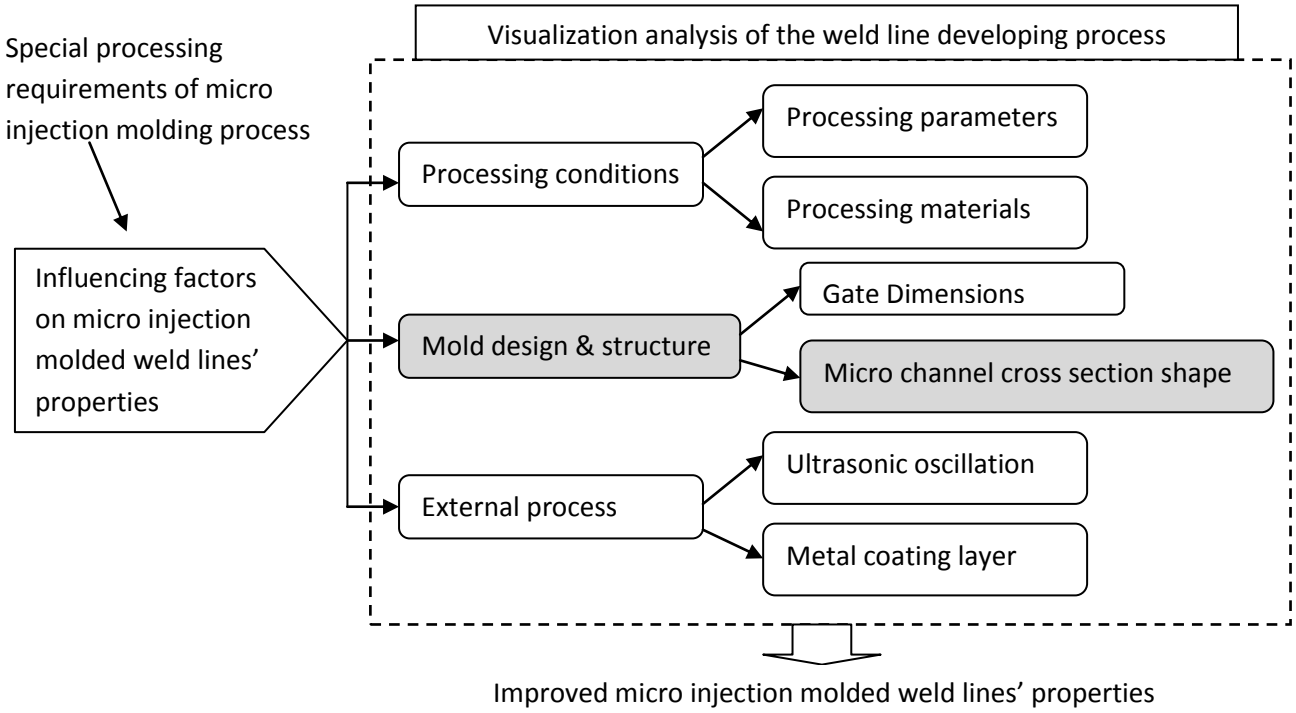
In order to investigate the correlation between cross section shape and weld line strength in different processing parameters of micro injection molding, a mold insert with multi-micro tensile bar cavities was machined by ultra high speed micro milling machine. And some related conclusions can be drawn as following:

1. According to experimental plan, the weld line micro tensile samples with different cross section shapes are injection molded and the weld line position and profiles are observed under microscope. Micro tensile sample with semi circle cross section shape has the best replication quality due to its relative big dimension than others;

2. Based on experimental results in different processing conditions, it can be found out that when the cross section shape is different, their corresponding weld line strength is also different. Equilateral triangle cross section contributes to strongest weld line, and then is trapezoid, semi-circle is the last;

3. The quantitative factor *a* reflecting cross section shape is defined, and higher *a* value related to stronger weld line strength, which is able be verified by the tensile test results for different cross section shape samples;

4. After weld line strength comparison in different processing conditions, the results show that higher injection pressure induced lower weld line strengths whatever the cross section shape is. Higher mold and melt temperature, equilateral triangle cross section gives better weld line strength than lower case. But mold and melt temperature affect weld line strength weekly for other cross section shapes.



Mold Design and Structure Factor II

8 Effects of gate dimensions on micro injection molded weld line strength

In the chapter finished above, one weld line influencing factor related to mold design and structure was discussed, in the following, another factor in the same area will be stated and explained, the effect of mold gate dimensions on micro injection molded weld line strength.

8.1 Experimental principle and setup

8.1.1 Principle

Gate type and dimension are actually the very import factors to influence the orientation of polymer molecule, filled particles and fibers, as well as the part mechanical and physical

properties in injection molding process. One injection mould with 4 micro tensile sample cavities was designed and constructed. Each cavity responses to different gate dimension. Those gate dimensions were specially chosen, in order to reveal the correlation between geometrical feature of the gate and the weld line strength (e.g. how the gate depth influences the weld line strength). The effects of gate dimension of the mould on mechanical properties of weld line were implemented in various processing conditions. Then the tensile test was used to characterize the micro injection molded weld line strength as before.

8.1.2 Injection mould design and manufacture

There are a lot of kinds of gate type, like step gate, film gate, edge gate and so on. The objective parts with rectangular cross sections are same as the one described in Chapter 5 (Fig.5-1a.). Considering the geometry and dimension of this micro tensile sample, the type of edge gate was chosen as the objective gate, the schematic drawing is shown as Fig.8-1. A double-gate four cavities mould was designed and constructed, and the four gate dimensions are separately used for each cavity, described in Fig.8-2. Those gates have the same length, but different width and depth. Gate Nr.1, Nr.2 and Nr.4 have the same depth but different width; Gate Nr.2 and Nr.3 have the same width and different depth; Gate Nr.3 and Gate Nr.4 have the same cross section area, listed in Table8-1. The four micro tensile cavities have the same geometry and dimensions as Fig.5-1a displayed.

According to the previous results achieved in the chapter before, in order to form the multi cavities micro tensile samples, a variotherm system was applied in this mould, shown in Fig.8-3. The heating method is by the electrical resistance heating bar and the cooling media is the cold water at 19°C.

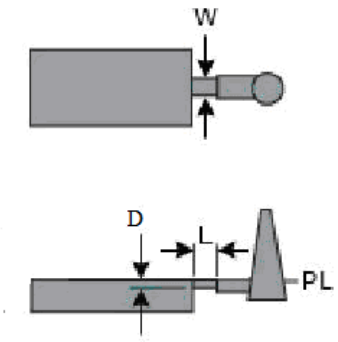
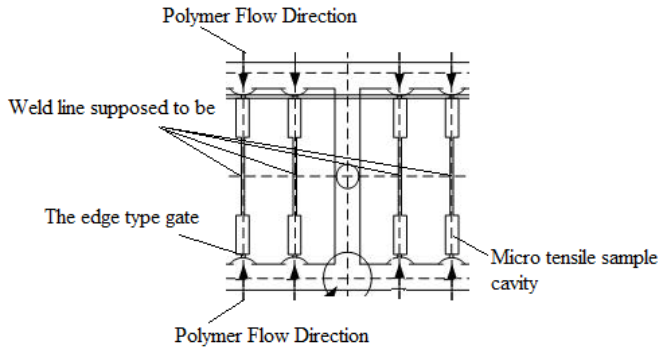
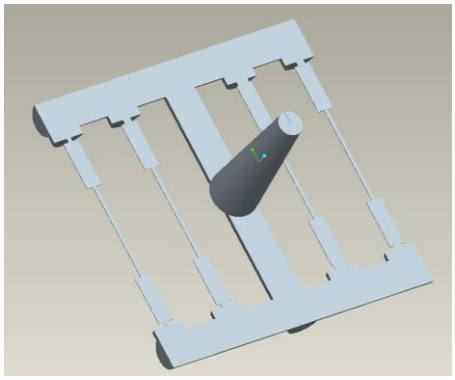


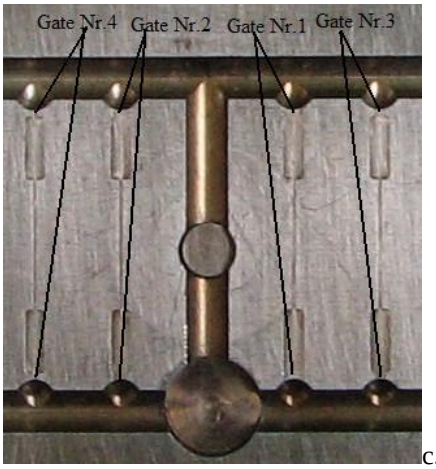
Fig.8-1. Schematic drawing of the edge gate type used in the experiment



a.



b.



c.

Fig.8-2 Multi-cavities mould constructed with different dimensional gates: **a.** Schematic drawing; **b.**3D model of the entire part; **c.** Real appearance of micro mold cavities

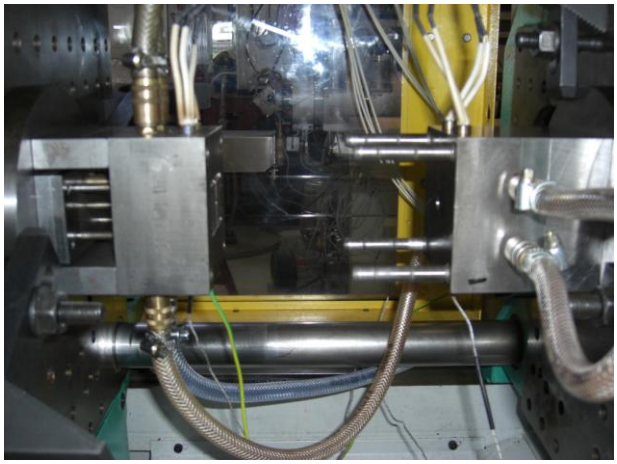


Fig.8-3 Variotherm system used during the micro injection molding process

Table 8-1 Gate dimensions used in the experimental mould

Gate Nr.	**1**	**2**	**3**	**4**
Width (mm)	1.5	1.0	1.0	0.5
Depth (mm)	0.1	0.1	0.05	0.1
Length (mm)	0.5	0.5	0.5	0.5

8.1.3 Experiment Plan

In the experiments, two different polymers, PP and HDPE were served as the processing materials (material properties are illustrated in Chapter 4 in detail), and the Arburg® 320C was the injection molding machine same as the chapters before. The micro injection molding experiments were complied based on the experimental plan for, listed in Table8-2 and Table8-3. The processing parameters (melt temperature, mold temperature, injection speed and injection pressure) are various, and packing pressure is always set as 80% of injection pressure and packing time is 5 seconds. The ejection temperature is constantly in 60°C, which cooled down by the variotherm unit from the relative higher mold temperature.

Table 8-2 Experimental Plan for PP

Experiment Nr.	T melt[℃]	T tool[℃]	Inj.Pressure [MPa]	Injection Speed[cm3/s]
1	**210**			
2	**220**	135	100	110
3	**230**			
4		**135**		
5	220	**140**	80	90
6				**70**
7	220	135	100	**90**
8				**110**
9			**80**	
10	220	135	**100**	110
11			**120**	

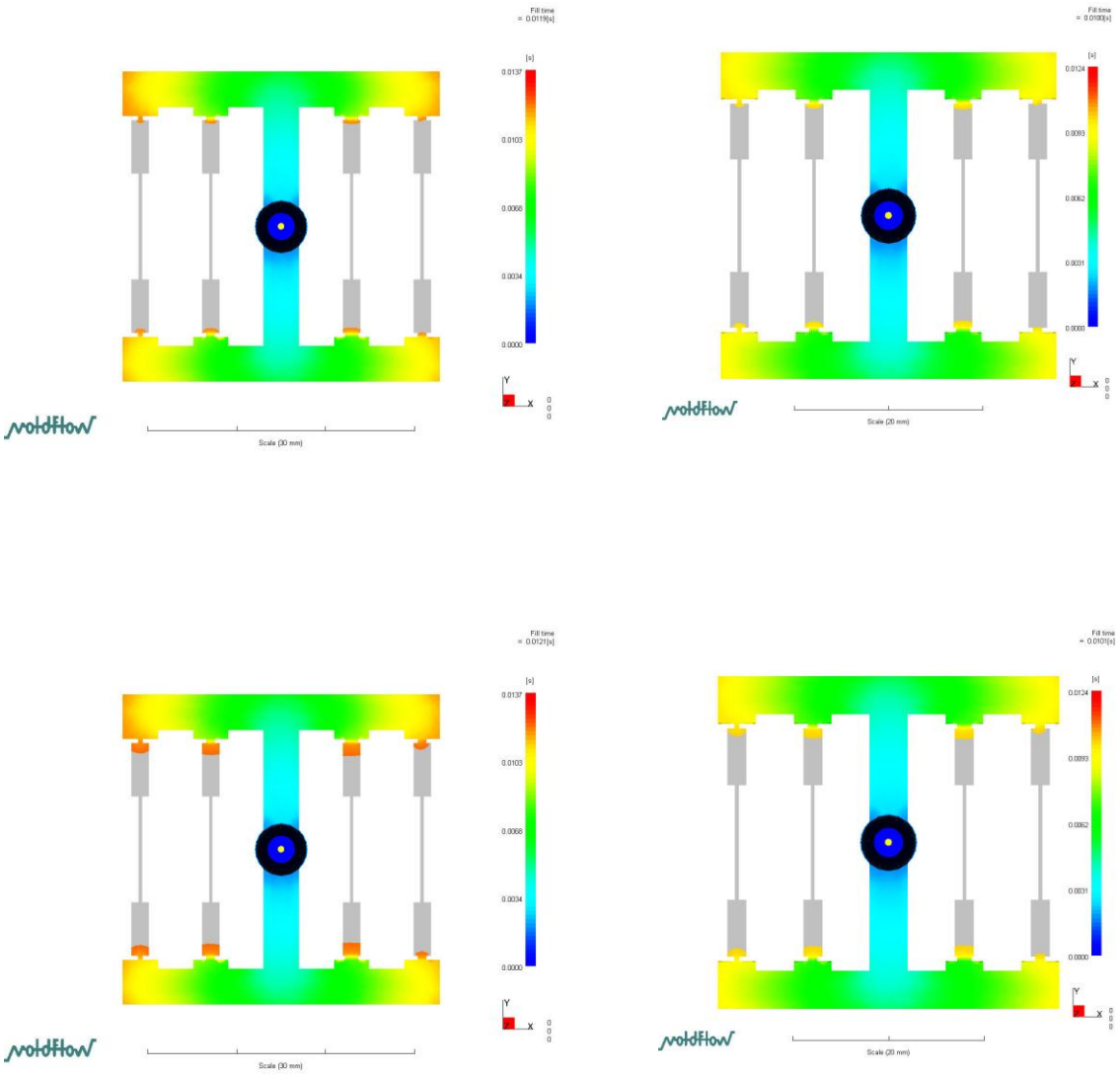
Table 8-3 Experimental Plan for HDPE

Experiment Nr.	T melt[℃]	T tool[℃]	Inj.Pressure [MPa]	Injection Speed[cm3/s]
1	**190**			
2	**200**	130	100	90
3	**210**			
4		**125**		
5	200	**130**	100	70
6		**135**		
7				**70**
8	200	130	100	**90**
9				**110**
10			**80**	
11	200	130	**100**	90
12			**120**	

8.2 Relation between gate size and micro weld line mechanical strength

8.2.1 Initial Simulation

In order to understand and observe the cavities filling process, the initial simulation study for PP and HDPE have been done. Fig.8-4 shows the results separately. From those simulation results, it can be found that the volumetric filling sequence of the cavities is Gate1, Gate2, and then Gate4, Gate 3 is the last one filled both of PP and HDPE. The filling time of HDPE is longer than PP, since it has higher viscosity than PP based on the rheological testing and MFI value.



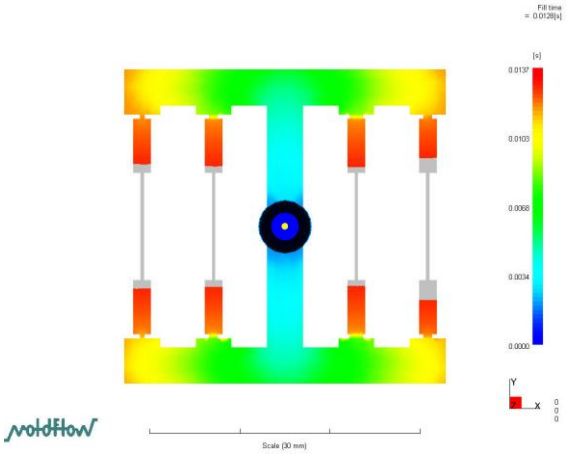


Fig.8-4a Filling process of the entire part for PP

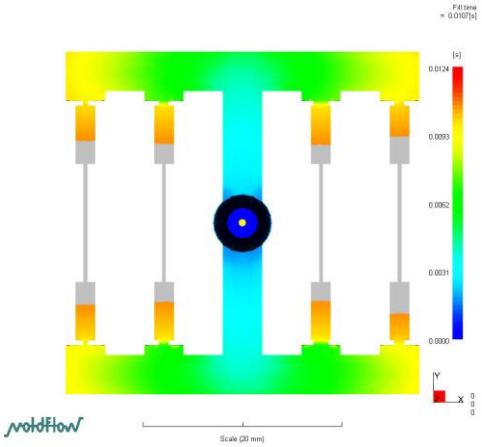
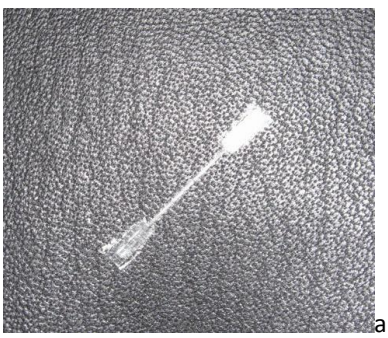


Fig.8-4b Filling process of the entire part for HDPE

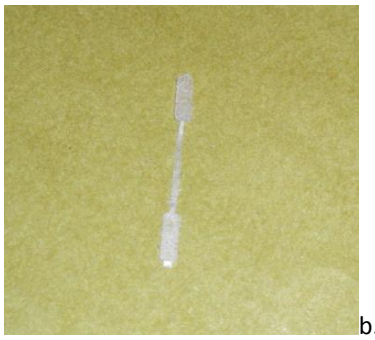
8.2.2 Analysis of the results

Through the micro injection molding process, the micro tensile samples with weld lines were prepared, which is displayed in Fig.8-5. However, there was a problem for HDPE, that is, the cavity related to Gate 1 was not able to be completely filled whatever the processing condition is. From the initial simulation results, Gate 1 is the most generous among of 4 gates and its corresponding cavity is always filled firstly. So it could be assumed that the cavity of Gate 1 must be blocked by the stick materials in the cavity during the HDPE samples preparation.

With the tensile test procedure described before, the corresponding ultimate breaking strength of weld lines by different gate sizes were measured and plotted in the following figures. Fig.8-6 till Fig 8-9 gives the results of PP and Fig.8-10 till Fig. 8-13 shows the results of HDPE.



a.



b.

Fig.8-5 the single sample of PP (a.) and HDPE (b.)

PP

Based on the results for PP, it is apparent that the relation between gate dimension and weld line strength is not liner. However, from Fig.8-6, one can find that except in the condition of

100 MPa injection pressure, with the changing of the injection pressure Gate.Nr.3 always response to highest weld line strength, followed by Gate.Nr.2. Gate Nr.1 and Nr.4 are in the end, they do not show obvious influence on the weld line strength. The same results are also displayed in Fig.8-9 in the different mold temperatures. In injection pressure 100 MPa, Gate Nr.3 and Gate Nr.2 response to almost equal weld line strength. When the injection speed and melt temperature are varying, Fig.8-7 and Fig.8-8 show that Gate Nr.2 leads to better weld line strength than others, followed by Gate Nr.3, and the influence level between Gate Nr.1 and Nr.4 is still not able to be obviously tell. When the gate depth is fixed (Gate Nr.1, Nr.2 and Nr.4), the gate with middle size width (Gate.Nr.2) gave the best weld line strength; When the gate width is fixed (Gate Nr.2 and Gate Nr.3), during injection pressure and mold temperature changing, the gate with smaller depth (Gate Nr.3) formed stronger weld line, conversely during injection speed and melt temperature changing, the gate with larger depth (Gate Nr.2) produced better quality weld line.

In addition, regarded as the correlation between processing parameters and weld line strength, Fig.8-6-Fig.8-9 show the same results as the authors' previous study gained in chapter 5.

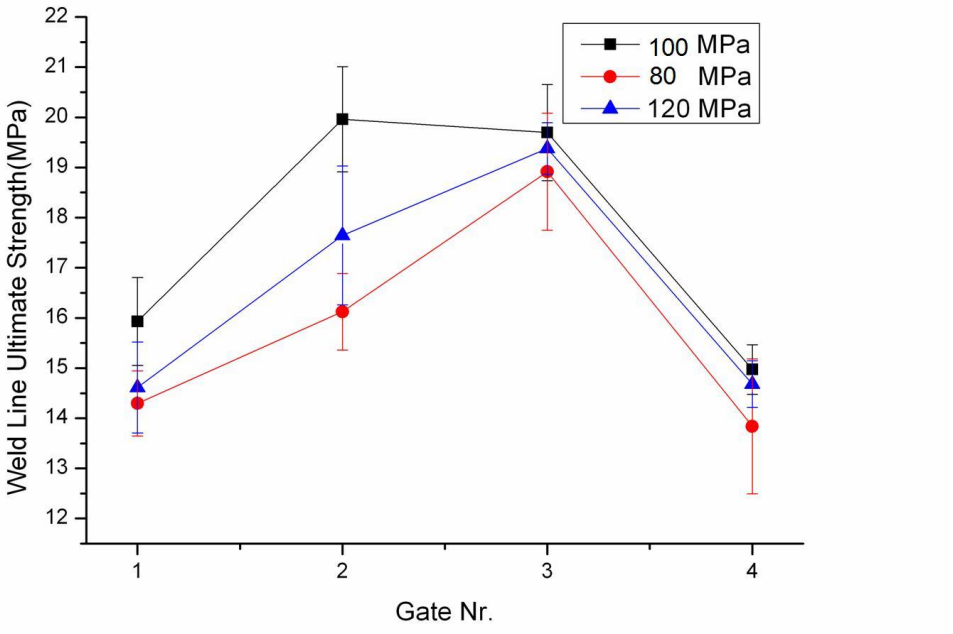


Fig.8-6 Weld line strength response to different gate size in 80,100 and 120 MPa injection molding pressure for PP, Melt temperature 220°C, Mold temperature 135°C and Injection speed 110 cm^3/s

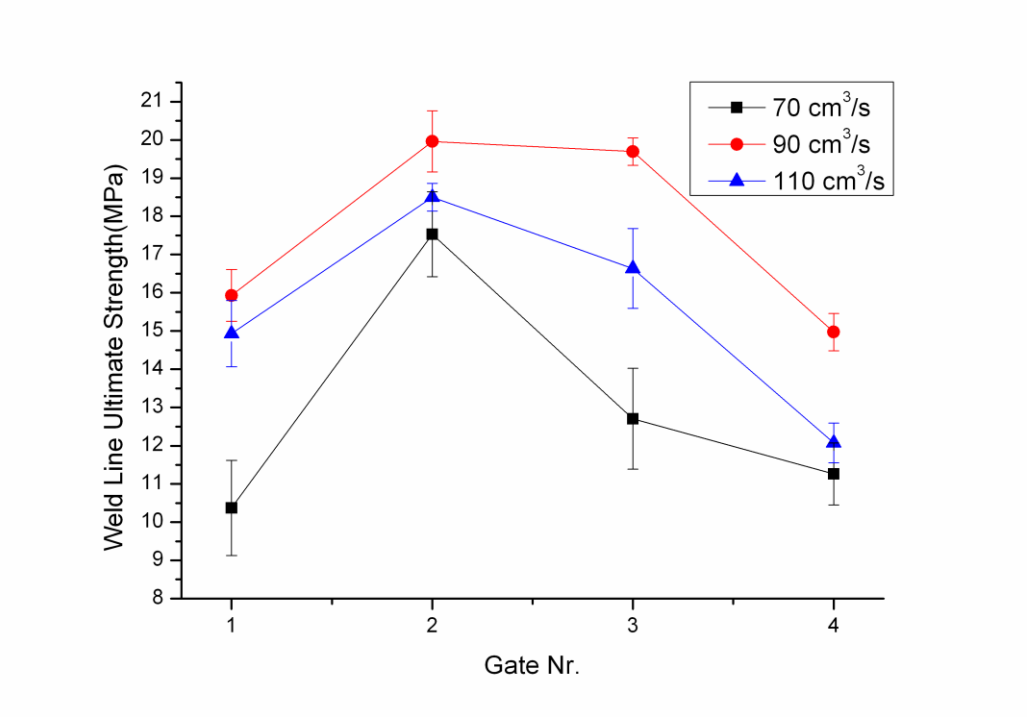


Fig.8-7 Weld line strength response to different gate size in 70, 90 and 110 cm3/s injection speed for PP, Melt temperature 220°C, Mold temperature 135°C and Injection pressure 100MPa

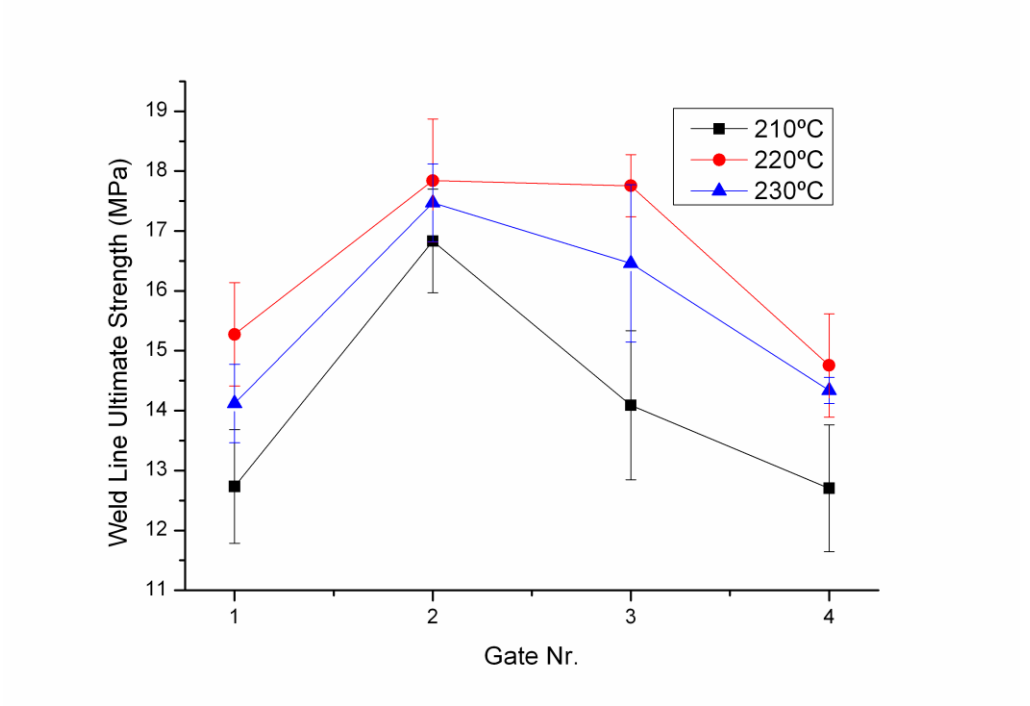


Fig.8-8 Weld line strength response to different gate size in 210, 220 and 240°C melt temperature for PP, Mold temperature 135°C, Injection speed 110cm3/s and Injection pressure 100MPa

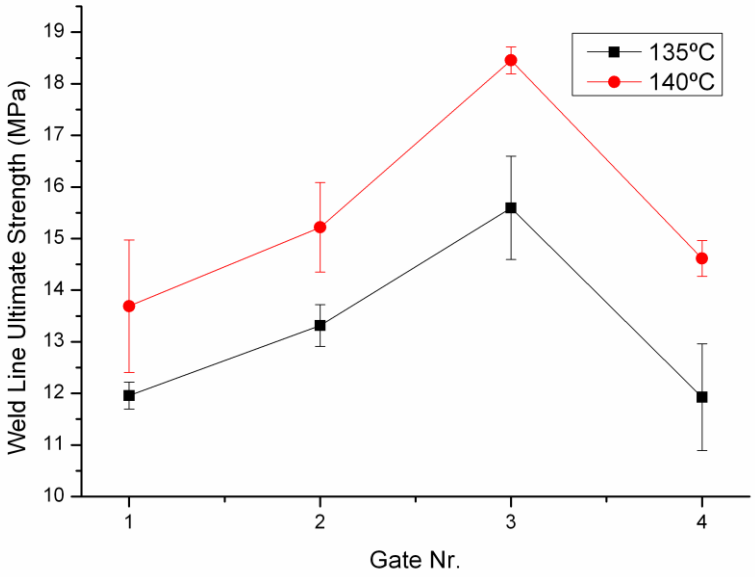


Fig.8-9 Weld line strength response to different gate size in 135 and 140°C mold temperature for PP, Melt temperature 220°C, Injection Speed 90 cm3/s and Injection pressure 80MPa

HDPE

From the test results of weld line for HDPE, Fig.8-10 presents that with the different injection pressures, Gate Nr.3 contributes to the best weld line strength which is same as PPs' results, but Gate Nr.4 is the second best instead of Gate Nr.2. Regarding to different injection speeds, mold temperatures and melt temperatures, the relation between gate dimensions and the weld line strength is same as the performance in different injection pressure. When the gate width is same, smaller gate depth causes stronger weld line; when the gate depth is same, still the smaller gate width leads to better mechanical property of weld line.

Furthermore, Fig.8-10 to Fig.8-13 also implies the effect of processing parameters on HDPE weld lines strength in micro injection molding. From Fig.8-10, 80 MPa injection pressure is more in favor to get stronger weld line, which means injection pressure influences the weld line strength not linear. The similar facts are also observed in Fig.8-11till Fig.8-13, there are intermediate optimal processing conditions leading to stronger weld line, when injection speed is 90 cm^3/s, Melt Temperature is 200 °C, Mold Temperature is 130 °C. Higher or lower parameter level could not obtain the best mechanical property for weld line in micro injection molding with HDPE.

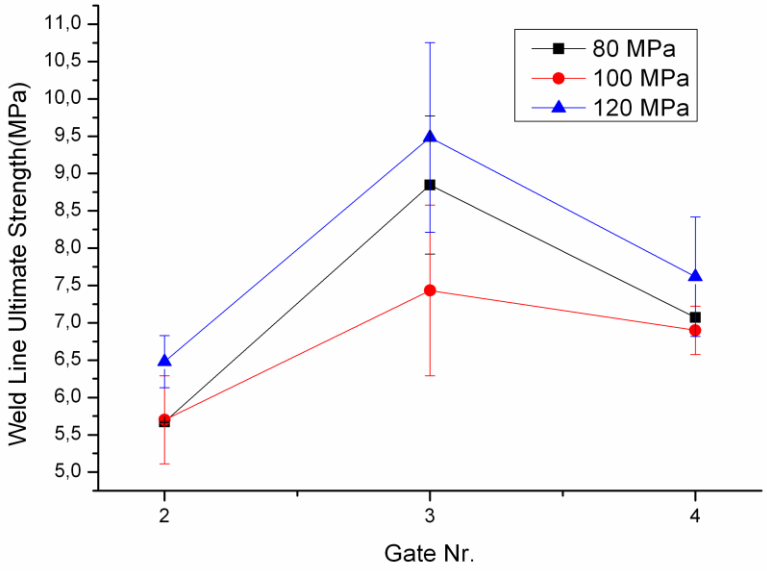


Fig.8-10 Weld line strength response to different gate size in 80, 100 and 120 MPa injection pressure for HDPE, Melt temperature 200°C, Mold temperature 130°C and Injection speed 90 cm^3/s

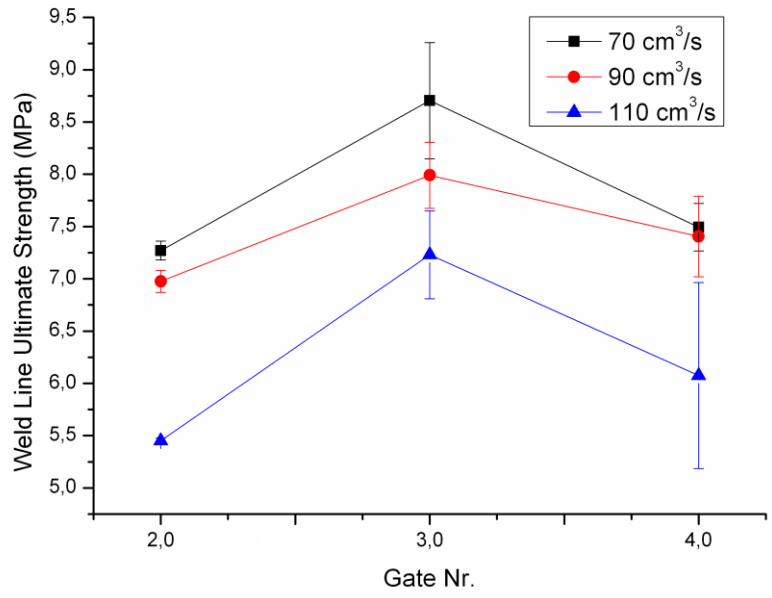


Fig.8-11 Weld line strength response to different gate size in 70, 90 and 110 cm^3/s injection speed for HDPE, Melt temperature 200°C, Mold temperature 130°C and Injection pressure 100MPa

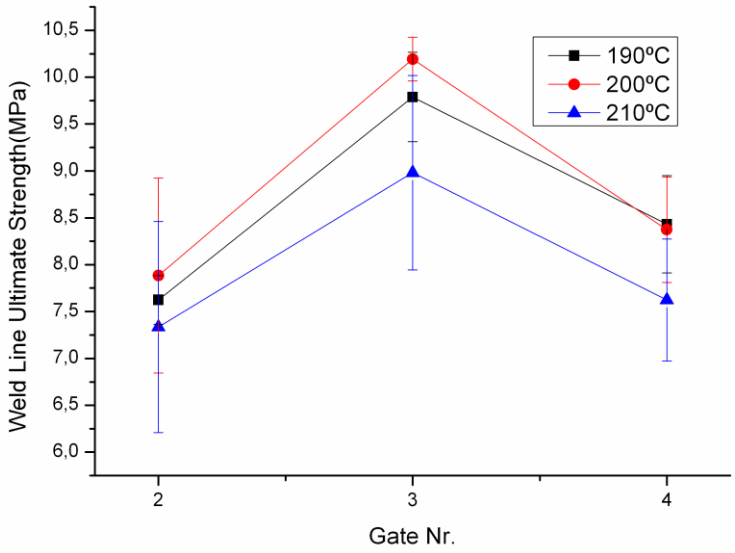


Fig.8-12 Weld line strength response to different gate size in 190, 200 and 210°C melt temperature for HDPE, Melt temperature 200°C, Mold temperature 130°C and Injection speed 90 cm^3/s

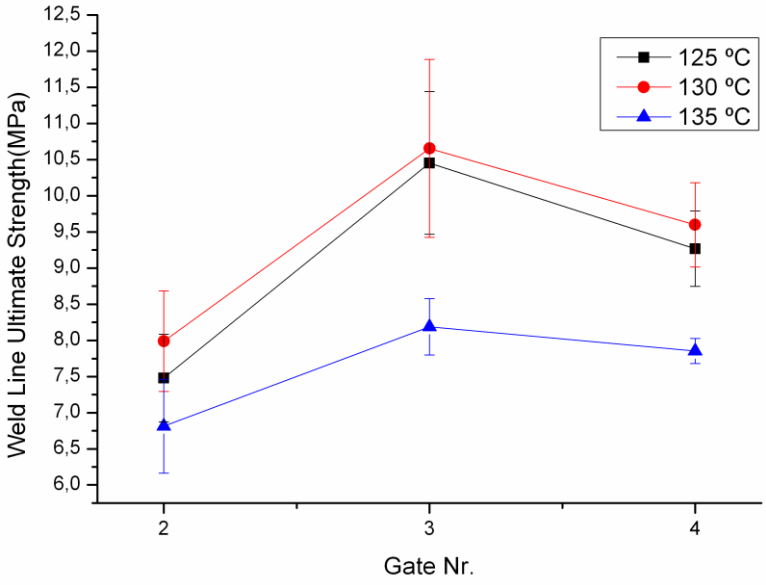


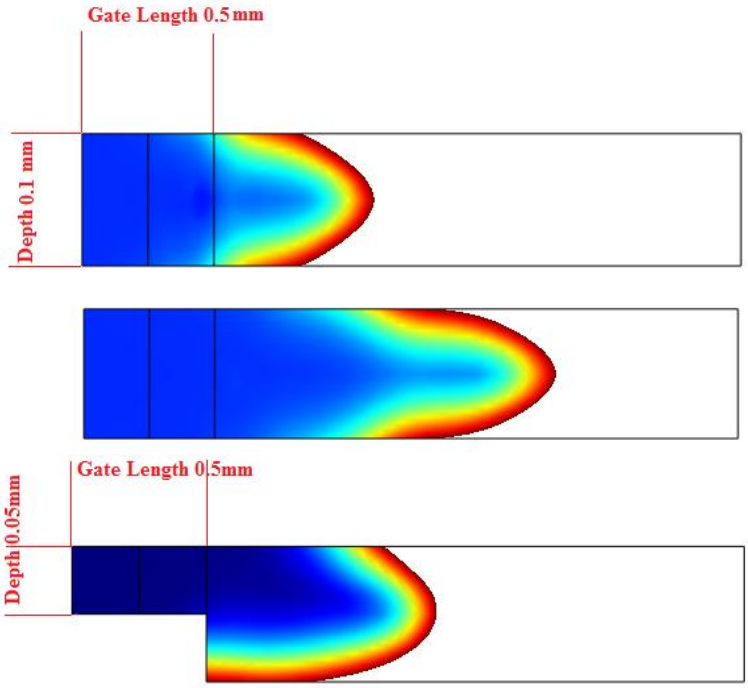
Fig.8-13 Weld line strength response to different gate size in 125, 130 and 135°C mold temperature for HDPE, Melt temperature 200°C, Injection pressure 100MPa and Injection speed 70 cm^3/s

8.2.3 Gate dimension effects mechanism analysis

From the results achieved above, it could be found that the width of the gate has a consistent influencing trend on the weld line strength for these two materials respectively, when the depth of gates are constant (0.1mm depth, Gate Nr.1, Nr.2 and Nr.4), for PP, whatever the

processing parameter varying, Gate Nr.2 always responses to the strongest weld lines strength and for HDPE Gate Nr.4 causes best weld lines strength, but the depth of the gate not always affects on the strength of the weld line always in the positive way (the strongest weld line related gate Nr. is different with the processing parameters). And bigger gate size not all the time contributes to stronger weld lines, which is different with the results in normal scale injection molding process. When the area of gates' cross section are equal (0.05 mm^2, Gate Nr.3 and Gate Nr.4), by the experimental results, it was convinced that the gate (Gate Nr.3) with larger width and smaller depth will create stronger micro injection molded weld lines.

The coupling effects of the edge gate depth are stronger than ones of the edge gate width. Because the varying range of the gate depth (0.05 mm and 0.1mm) is in the same magnitude scale with the thickness of the micro tensile part used here (0.1 mm), the flow behavior of polymer melts in this micro scale will be influenced in thickness direction dramatically. On the contrary, the effect of the gate width variation is gentler. This can be supported by the simulation results: In Fig.8-4, the effect of gate width variation on polymer filling in micro cavities is performed. And Fig.8-14 shows how the gate depth impacts on the flow fronts, which executed the simulation of flow front shapes advancing when the depths of the gate are 0.05mm and 0.1 mm. After comparing the simulation results, it can be found that the variation of gate depth impact the flow front shape more dramatically than the width variation's case. The influencing mechanism of flow front shape on weld line strength is schematically shown in Fig. 8-15 [123-124].



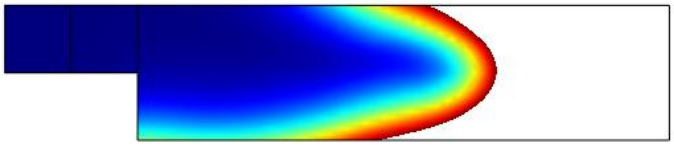


Fig.8-14 The simulating flow front shapes in different gate depth and filling moment (0.1mm and 0.05mm)

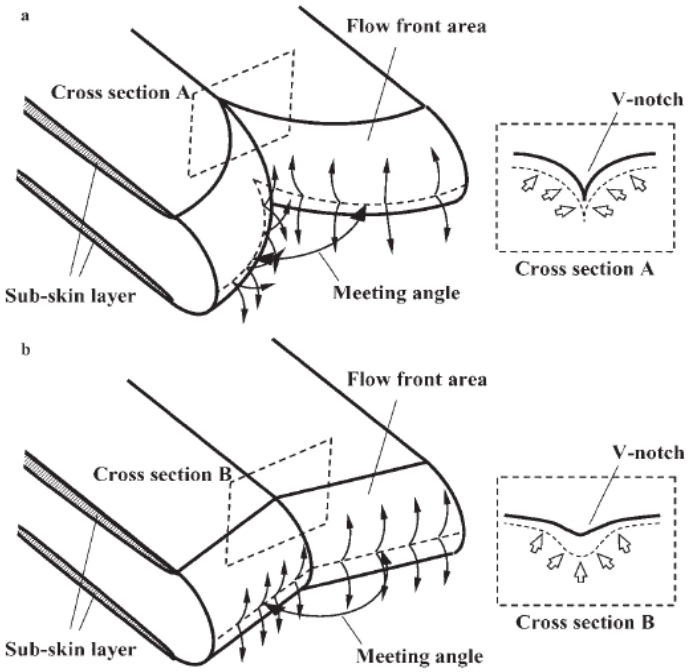


Fig.8-15 The principle that the flow front shape influencing the V notch size which the main factor deciding weld line strength[124]

The gate depth also gives an obvious impact on the morphology structure of the micro injection molded parts, which is intensively related to the strength of the weld line. The photo observed under the polarized microscope show the morphology of the materials along the thickness direction of the sample (in Fig.8-16), there are only skin layer and shear structure and no core layer like normal size injection molding parts (in normal size injection molding process parts, the core layer occupied the main portion of the material microstructures). This kind of morphology structure in micro injection molding is more easily affected by the processing condition related to flow behavior. For example, the thickness of skin layer is sensitively related to temperature condition, and the shear structure is closely related to injection speed and pressure. Therefore, the weld line strength is more sensitive to the coupling effects of depth varying of the gate and processing parameters on PP as well as on HDPE.

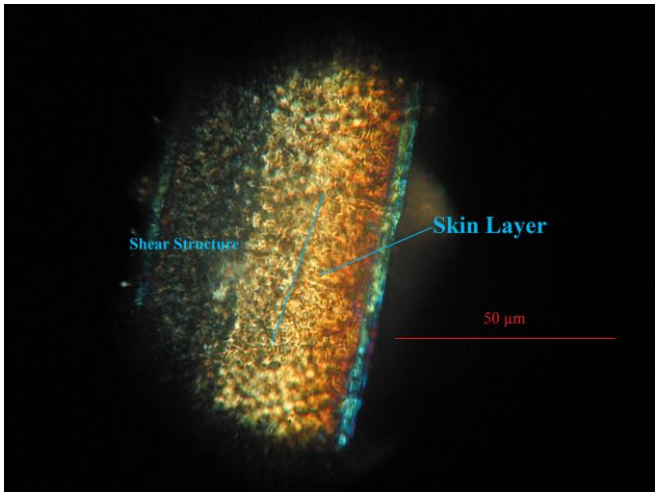
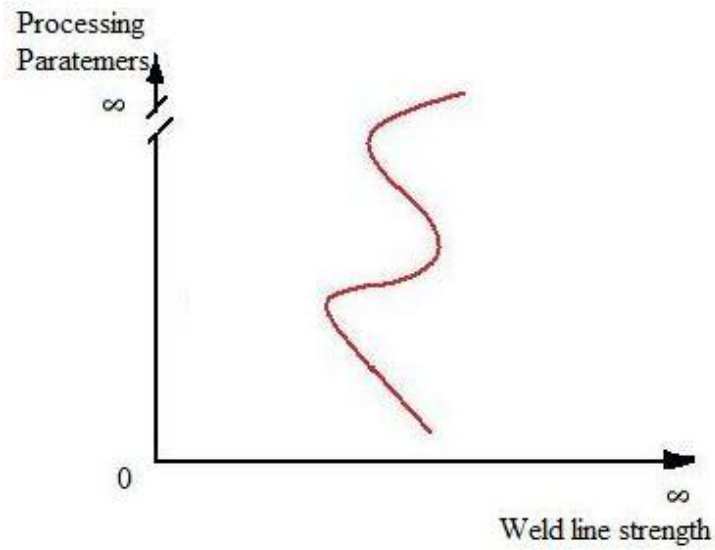
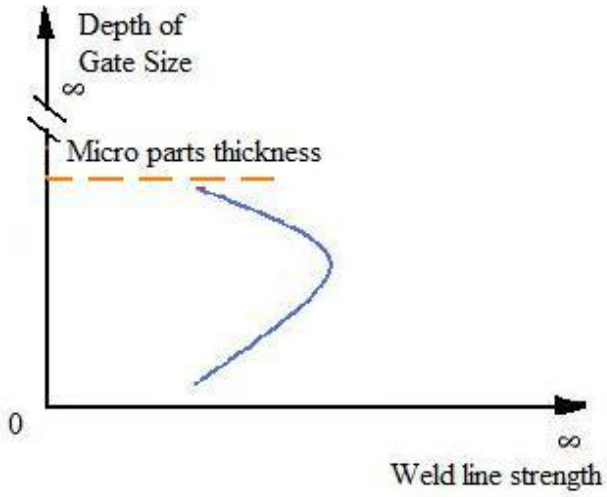


Fig.8-16 The morphology of micro injection molded tensile sample in the thickness direction under polarized microscope



a.



b.

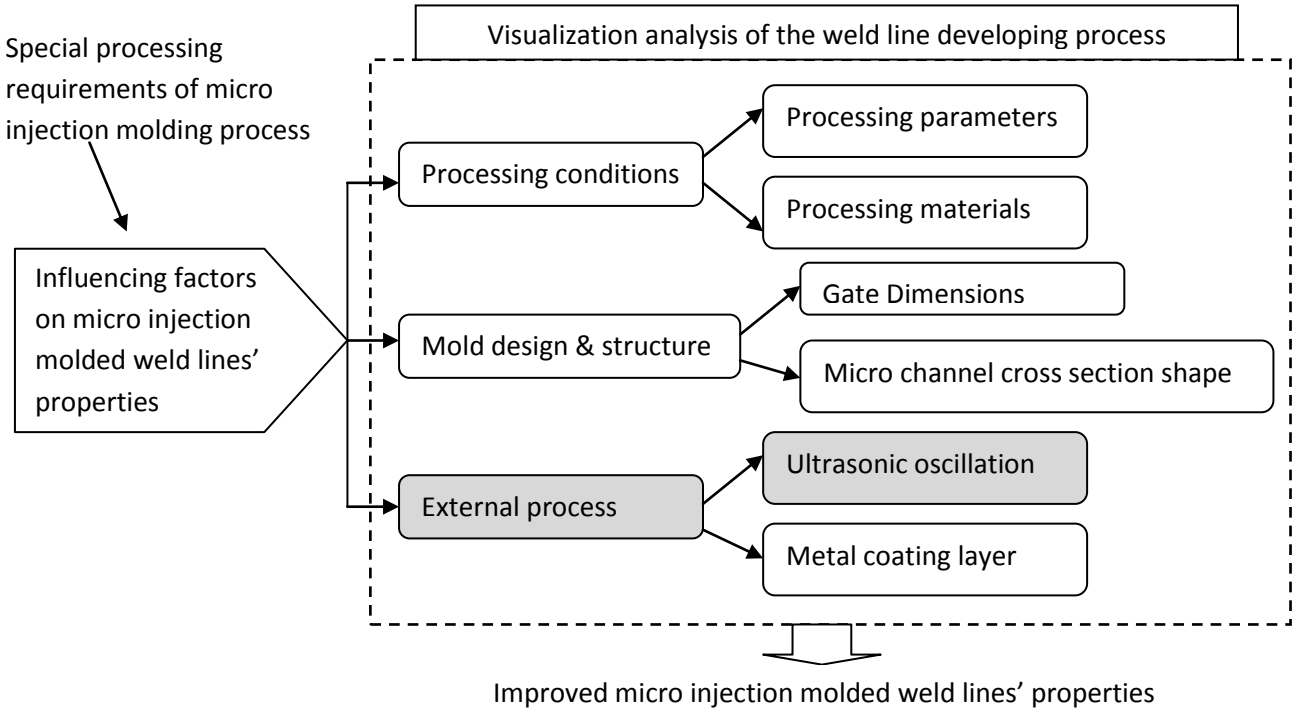
Fig.8-17 the trend curve describing the correlation between **a.** processing parameters, **b.** gate size and the weld line strength

Based on these results for the correlation of weld line strength, gate size and processing parameters, a trend curve to describe it was proposed like Fig.8-17, in which the relation between processing parameters and weld line strength is "Multi-**S** wave" profile, which means the optimal point for processing parameters will not be unique and fixed; And the depth of edge gate relates to the weld line strength by a Parabola profile. However, more verifying researching works need to be proceeded in future in this aspect.

Summary

According to the investigated experimental results, about the injection mould gate dimension influencing weld line strength in micro injection molding, the following conclusions could be drawn:

1. The gate dimension definitely has effects on the weld line strength in micro injection molding process. And this effect is coupled with processing conditions;
2. For PP material, when the gate depth is equal (Gate Nr.1, Nr.2 and Nr.4), the gate with middle size width (Gate.Nr.2) has the best weld line strength; When the gate width is equal (Gate Nr.2 and Gate Nr.3), with the changing of injection pressure and mold temperature, the gate with smaller depth (Gate Nr.3) responds to stronger weld lines, on the contrary with the changing of injection speed and melt temperature, the gate with bigger depth contributes to better weld line quality;
3. For HDPE material, the cavity corresponding to Gate Nr.1 cannot be completely filled, perhaps due to the cavity blocking of the stick materials and dirt. As for the other 3 gates, Gate Nr.3 always leads the best weld line strength; the following is Gate Nr.4 and then is Gate Nr.2.



External Process Factor I

9 Ultrasonic improvement of micro injection molded weld line strength

In real industrious production, during or after the injection molding process, some external assistant process or treatment can affect the weld lines' strength, for examples, ultrasonic oscillation assistance during the injection molding process. Since the ultrasonic oscillation can stimulate the vibrations and activation of the polymer molecular chains without additional heating, this clean, reliable and efficient technology was fast spread and developed in polymer plastifing, mixing and welding fields[125-130]. In the section, the mechanism and effect of ultrasonic oscillation on micro injection molded weld line strength were investigated.

9.1 Experimental principle and setup

9.1.1 Principle

The micro dog-bone tensile test sample same as the one always used in previous research was selected as the objective part. The micro part was prepared by the double gate injection mold which is able to form an intending weld line in the middle of the tensile sample. Additionally, the ultrasonic generator was integrated in this mold in order to investigate the effect of ultrasonic oscillation on the micro injection molded weld line strength. The micro samples with weld lines were produced in different ultrasonic out power/working time and measured by tensile test, so that how the ultrasonic output power and the oscillation inducing time affect the weld line strength can be revealed.

9.1.2 Ultrasonic experimental setup

An ultrasonic oscillation generator with sonotrod was integrated within the injection mold. The output power of the ultrasonic equipment is adjustable and it can reach 800W at its maximum. The working frequency is 20 KHz. The sonotrod was assembled directly above the micro cavity, which make the ultrasonic oscillation transmitted to the polymer melts in micro cavity in the best way. When the ultrasonic device works, the sonotrod will generate the ultrasonic oscillation in the frequency of 20 KHz. This can result in the same oscillation in injection mould cavity, which will drive the polymer melts oscillation during the injection molding process. The schematic structure of the experimental device is shown in Fig.9-1. The real appearance of the whole ultrasonic oscillation set-up is displayed In Fig.9-2. Additionally, a variotherm unit was constructed in this mold to satisfy the control requirement of rapid heating and cooling the mold.

9.2 Experimental results and discussion

9.2.1 Micro injection molding experiments coupling ultrasonic oscillation

In order to investigate how the ultrasonic output power and the oscillation inducing time affect the weld line strength, there were three output power levels to be chosen (400W, 600W and 800W). The oscillation is induced in two different moments: 1. the oscillation is induced from injecting moment to ejection moment, named as Mode 1; 2. the oscillation is induced from injecting moment to packing procedure finishing, named as Mode 2.

The other processing parameters are constant during samples preparation: the injection pressure is 100MPa, the injection speed is 100cm^3/s, the mold temperature is 150°C, the melt temperature is 240°C and the ejection temperature is 60°C.The micro injection molded tensile sample is illustrated in Fig.9-3, as well as the broken sample after tensile testing.

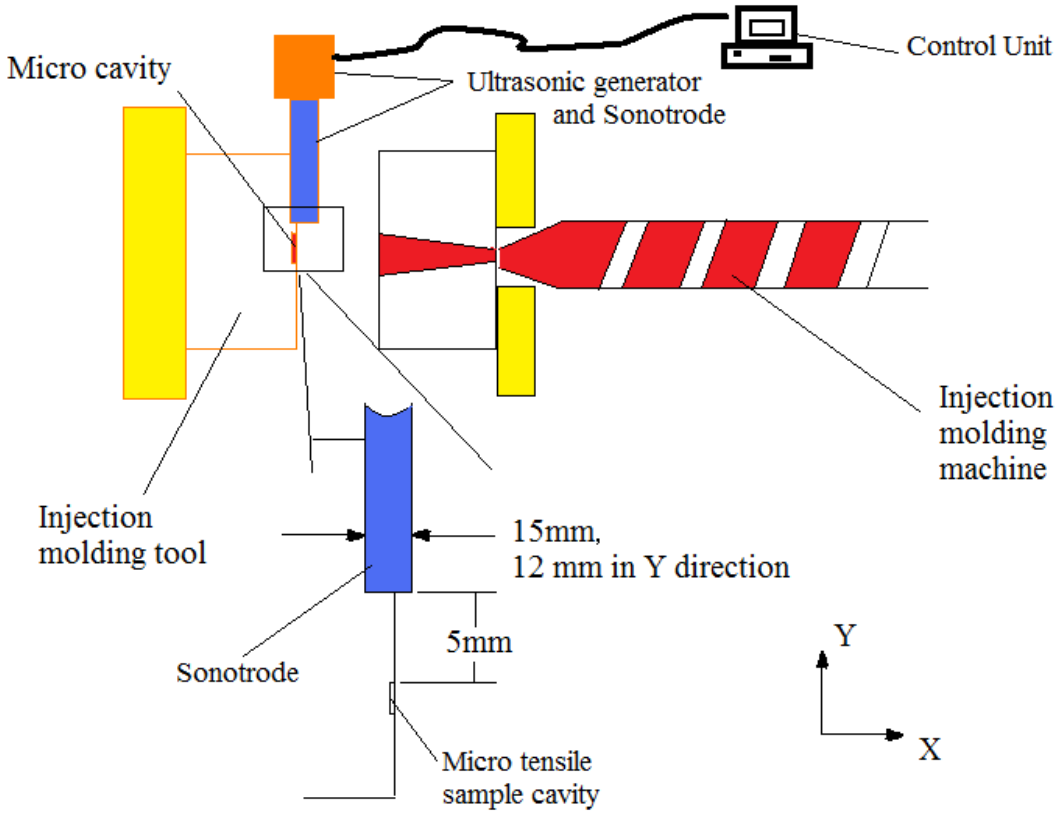


Fig.9-1 The schematic figure of the whole experimental device


a.


b.

Fig.3a Real assembly appearance of the ultrasonic integrated injection molding tool;
Fig.3b the Control unit of the ultrasonic generator

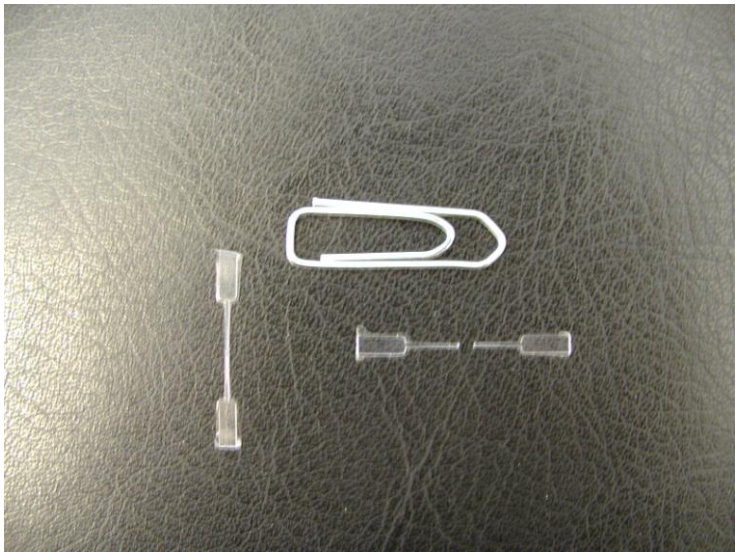


Fig.9-3 The micro injection molded tensile sample before and after tensile test

9.2.2 Analysis of the results

The weld line tensile stresses of the samples in different ultrasonic reinforcing conditions are plotted in Fig.9-4. From Fig.9-4, it can be found that the ultrasonic oscillation generally reinforced the micro injection molded weld lines. The tensile stresses of the weld lines with ultrasonic functions are 8.32%-24.1% higher than the ones without ultrasonic assistant, which indicates that the weld line strength in micro injection molding can be well reinforced by the ultrasonic oscillation due to the fact that ultrasonic oscillation induces better diffusion among the melting polymer molecular.

In addition, the ultrasonic working mode 1 gives better effects than mode 2 in all ultrasonic output power varying range. This result is converse to the results reported in the literature for the macro injection molded weld line. In their results, the ultrasonic oscillation induced after packing procedure will give a worse performance than the case of stopping the ultrasonic in packing procedure because after the packing step the polymer melts solidified very fast due to the big temperature difference between the mold and the melts and the ultrasonic oscillation will break the solidified connection in weld lines area. However, in this study case, a variotherm unit was integrated in the mold which will make the melts solidified relative slower than the normal injection molding process and give more time to polymer molecular' inter diffusion by ultrasonic oscillation.

Another fact shown in Fig.9-4 is that when the output power is 400W, the corresponding weld lines strength are the best, especially in working mode 1, the improvement is more obviously. It implies that higher output ultrasonic power cannot lead to stronger weld lines. The possible reason is that the optimal orientation of the molecular structure for higher weld

lines strength could be disturbed by too high ultrasonic oscillation energy, even higher power is helpful for the entanglement of polymer melts.

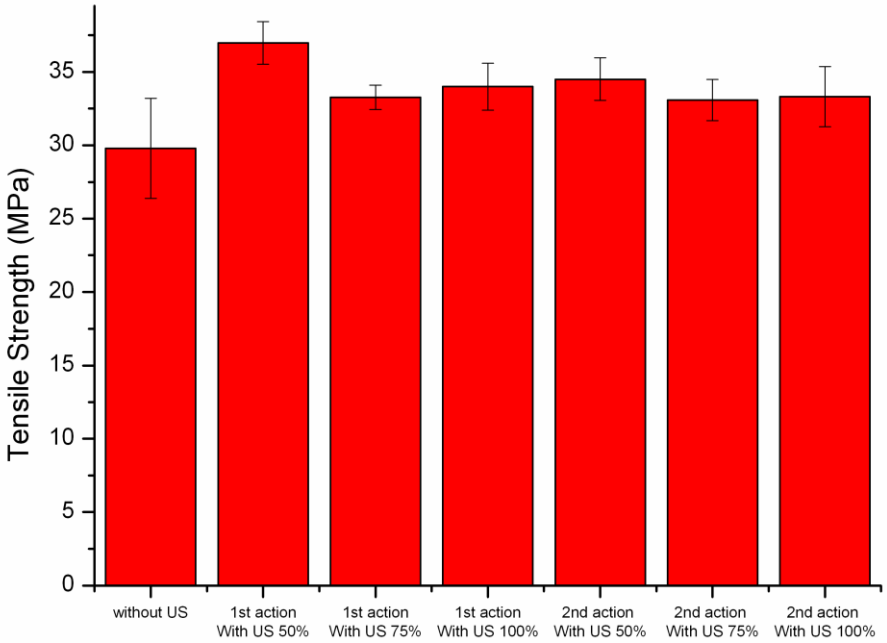
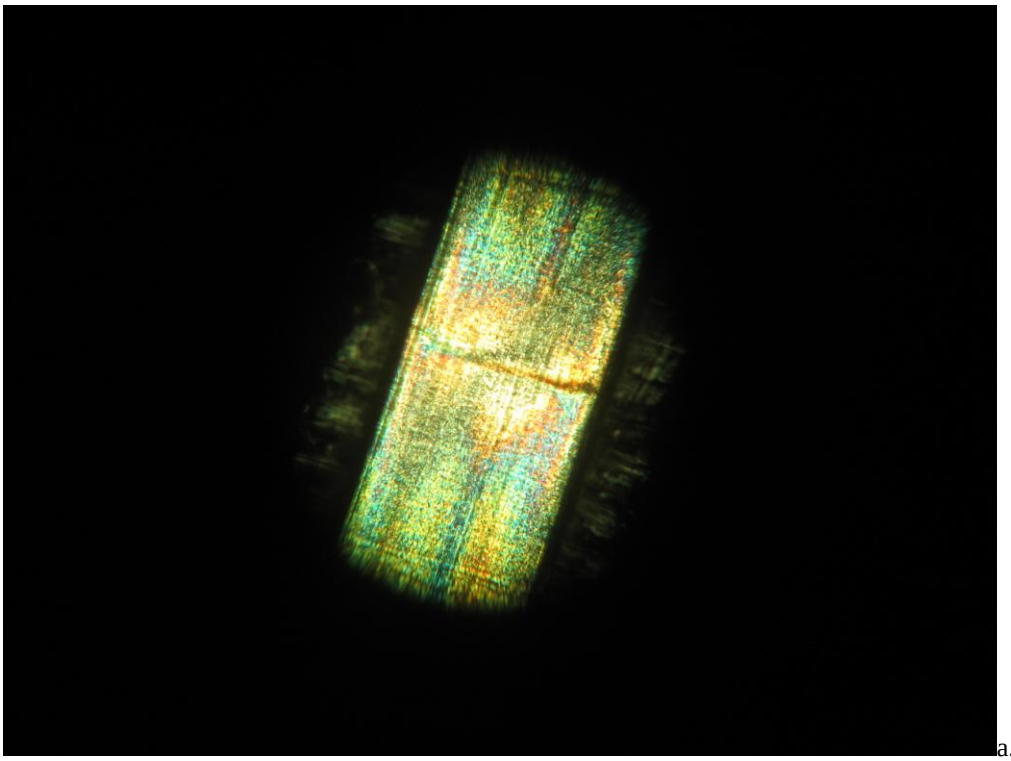


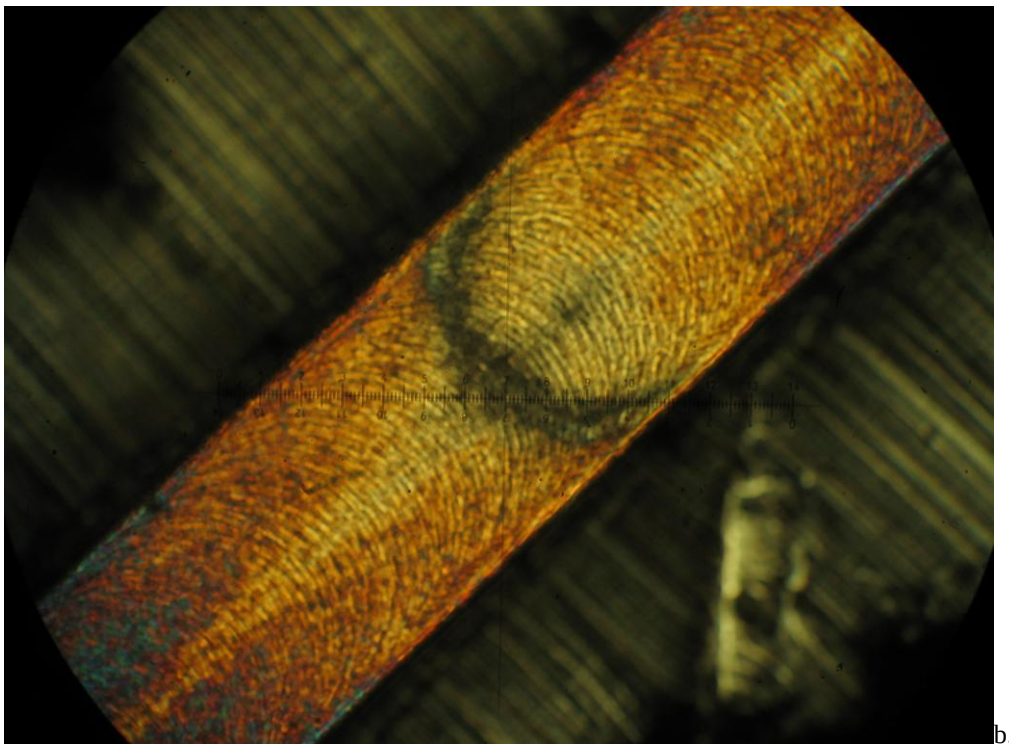
Fig.9-4 Weld line tensile stresses of the samples in different ultrasonic reinforcing conditions

In order to find out the mechanism of ultrasonic oscillation on micro injection molded weld line strength, the polarization microscope and atomic force microscope (AFM) were applied to analyze the weld line V notch profile. In Fig.9-5, the weld lines appearance of specimen without ultrasonic oscillation and with 400W ultrasonic oscillation under polarization microscope are illustrated separately. In the case without ultrasonic oscillation the weld line is a straight line which is perpendicular to the melts flowing direction, on the contrary, in the case with ultrasonic oscillation the weld line is a curve which should be formed when one flow front flew into the other. Obviously, the latter weld line with a curve profile should have better binding effects, since it gives more connection area. The Fig.9-6 shows the V notch profile of two weld lines respectively gained by AFM. The V notch with about 1 micro meter depth was found in the he specimen without ultrasonic oscillation assistant, but there are not the V notch could be detected in the specimen with ultrasonic oscillation. Through the optical microscopic observation, on the surface of the sample, the V notch was also not able to be observed clearly. It implies that the ultrasonic oscillation help the polymer melts from two directions adequately entangle each other. Especially in the area near the cavity wall, the ultrasonic oscillations delay the polymer melts solidification and make the frozen layer much

thinner than the case without ultrasonic induced. This leads to higher tensile strength of the micro injection molded weld line.

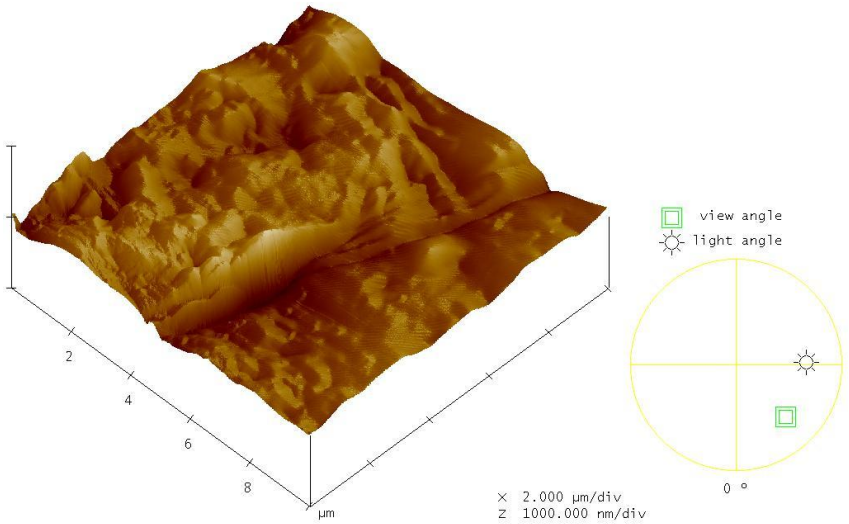


a.

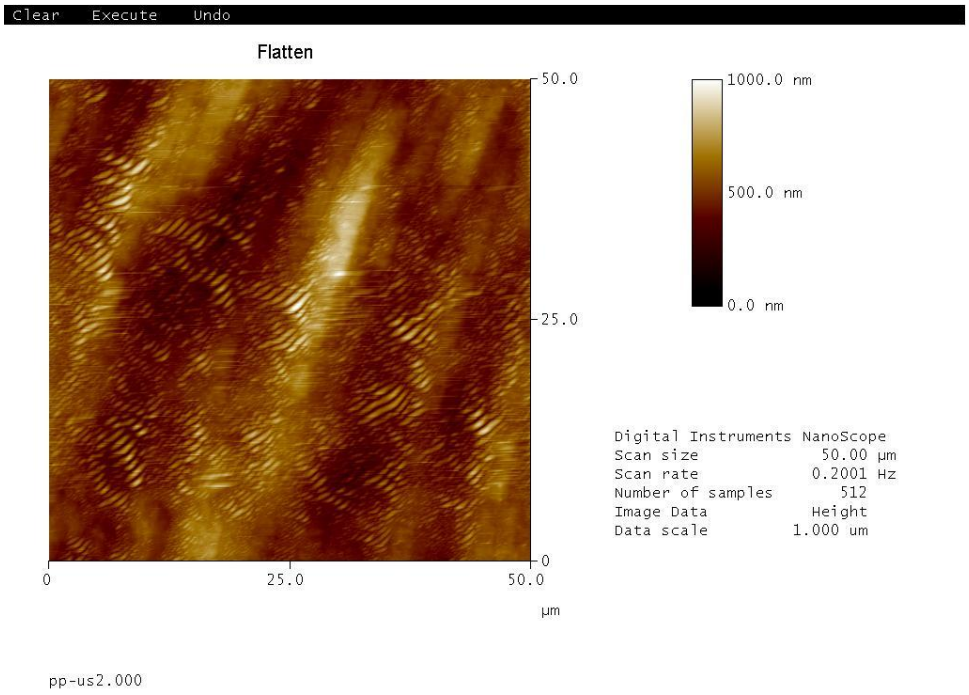


b.

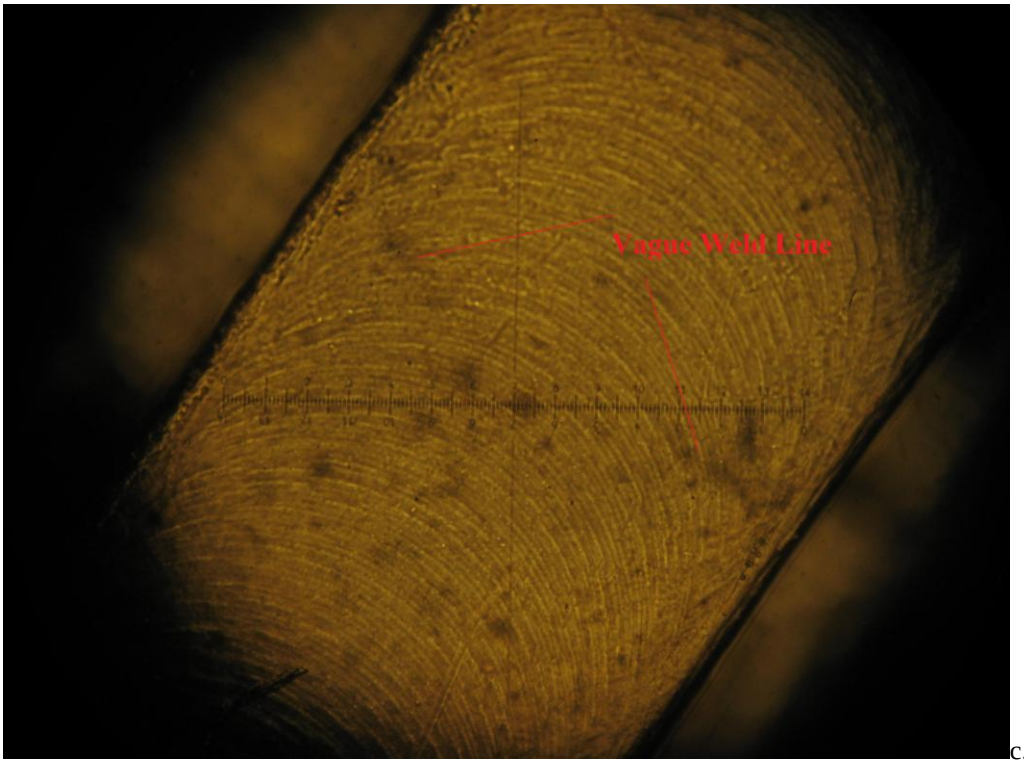
Fig.9-5a. Weld line of micro tensile sample without ultrasonic oscillation;
Fig.9-5b. Weld line of micro tensile sample with ultrasonic oscillation


view angle
light angle
2
4
6
8
µm
0 °
X 2.000 µm/div
Z 1000.000 nm/div
naht.002

a.


Clear
Execute
Undo
Flatten
50.0
25.0
0
0
25.0
50.0
µm
1000.0 nm
500.0 nm
0.0 nm
Digital Instruments NanoScope
Scan size 50.00 µm
Scan rate 0.2001 Hz
Number of samples 512
Image Data Height
Data scale 1.000 um
pp-us2.000

b.



c.

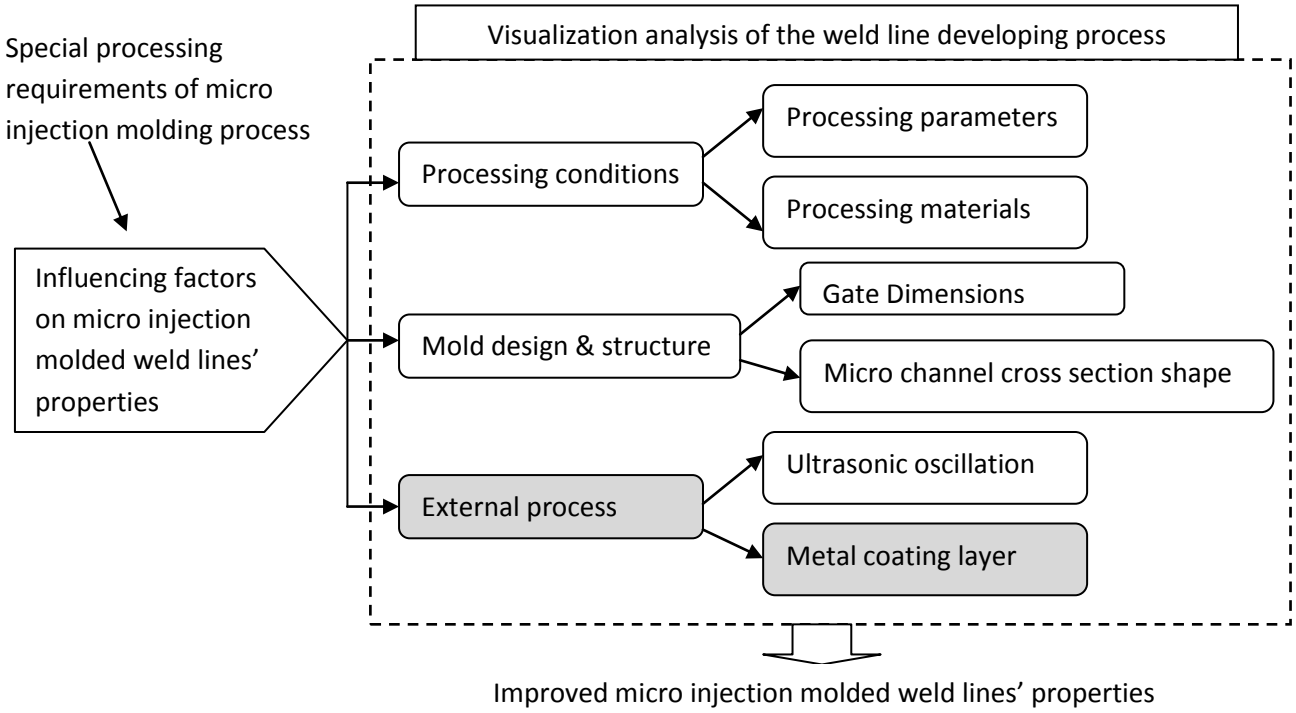
Fig.9-6a. V notch profile of the weld line without ultrasonic oscillation; b. V notch profile of the weld line with ultrasonic oscillation; c. The vague weld line on the surface of the micro tensile sample with ultrasonic oscillation effect

Summary

Based on the experiments of the ultrasonic oscillation function on micro injection molded weld lines strength, some conclusions can be drawn:

1. The ultrasonic oscillation is able to be used to reinforce the weld line strength in micro injection molding process with a good performance;
2. Two ultrasonic inducing modes were introduced and investigated in this study: Mode1. the oscillation is induced from injecting moment to ejection moment and Mode2. the oscillation is induced from injecting moment to packing procedure finishing. Tensile test results show that mode 1 gives better effects than mode 2 in all ultrasonic output power varying range;
3. Three ultrasonic output power levels were set: 400W, 600W, 800W. In both Mode 1 and Mode 2, 400W ultrasonic output power always contributes to the best improved weld line strength;
4. The influencing mechanism of the ultrasonic oscillation on micro injection molded weld line was analyzed. With the ultrasonic oscillation function, the weld line appeared as a curve which means one flow front flew into the other flow front. Additionally, the ultrasonic oscillation almost erased the V notch in weld line area according to the AFM

test and optical microscope observation. The curving weld line and almost disappeared V notch are supposed to be the reason for the reinforcement of the micro injection molded weld line strength with ultrasonic oscillation.



External Process Factor II

10 Effects of coating layer of micro parts on the weld line strength

In normal injection molded parts, heading to get the functional layer, improve mechanical properties or decorate the surface of polymer parts, they are coated with various metallic or polymeric layers after polymer processing. While regarding to micro injection molded polymeric parts, the metallic coating layers/ thin films with special electrical, magnetic and mechanical properties always are adhered on the micro polymer parts' surface, satisfying with the MEMS's multi-functional demands by chemical vapor deposition(CVD), physical vapor deposition(PVD) and electroforming etc. [130-134]. However, in the mean time when the parts' electrical and magnetic features are changed, their mechanical properties are modified

as well due to the varying of stress distribution from these external coating layers. Therefore, considering whether those functional coating themselves could possibly work as an enhancing element for polymer parts, especially for the weld line defect and aiming to reveal the mechanism of functional coating layer affecting weld line strength in micro injection molding, this chapter was planned and executed based on coating the micro injection molded tensile samples with intended weld lines by physical vapor deposition (PVD) technique.

10.1 Experimental principle and methods

10.1.1 Principle

The micro tensile test samples with proposed weld lines used in previous chapters were formed by micro injection molding process. Then they are coated with 2 kinds of metals in various layer thicknesses. The samples with and without coating layers were accessed by tensile test. Comparison between the cases with and without coating layer was implemented as well as among different coating conditions (coating material and layer thickness). Finally, the effects of coating layer on the weld line strength in micro injection molding were clarified.

10.1.2 Experimental Methods

Micro tensile sample preparation with weld lines formed by micro injection molding

The preparation procedures of micro tensile specimen are the same as before: the injection molding machine Arburg® 220S was processing equipment and the processing parameter were fixed as the following: Injection pressure 120 MPa, Injection Speed 20 cm3/s, Melt Temperature 230°C, mold temperature 130°C and ejection temperature 60°C.

Physical vapor deposition (PVD) coating

The physical vapor deposition (PVD) was employed as the thin film coating methods. The two typical metal coating materials, Aluminum and Titanium, were deposited in 3 thickness levels (400μm, 600μm and 800 μm) on one side of the molded weld line samples' surfaces.

PVD used in the presented study was based on the evaporation principle, which consists of a vacuum chamber, diffusion pump, samples holder/work plate, crucible and a shutter, schematically illustrated in Fig.10-1. The metal to be deposited is placed in the crucible, which will be heated by a tungsten filament or an electron beam to flash evaporate the coating metals and condense them on the surface of objective samples. Before the evaporating/depositing process, the vacuum chamber will be evacuated to a pressure of 2~5 × 10^{-6} torr. The thickness of the coating film is associated with the length of time that the shutter is opened and able to be measured and controlled by a Quartz Micro Balance (QMB)-

based film thickness monitor. For materials with a rather low melting temperature, like aluminum, the tungsten filament was served as the heating method. For metals with higher melting temperature, like titanium, the electron-beam was considered as the heating method, and in this article, the titanium is heated by an electron beam with a power of 4.2 keV. Fig.10-2 shows the micro tensile samples with the coated thin films.

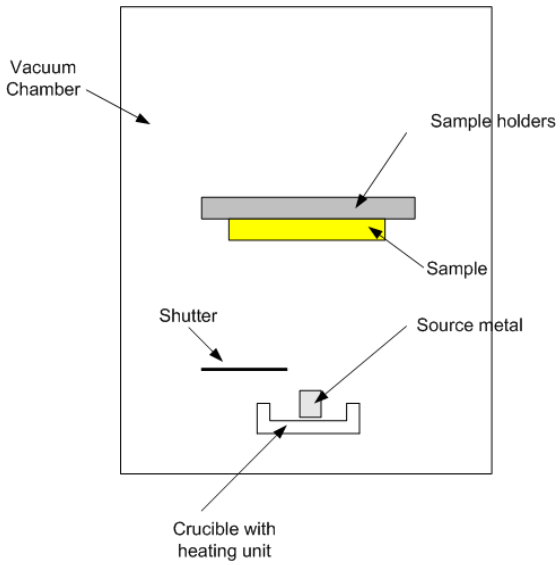


Fig.10-1 Schematic of the PVD equipment in thermal evaporation principle

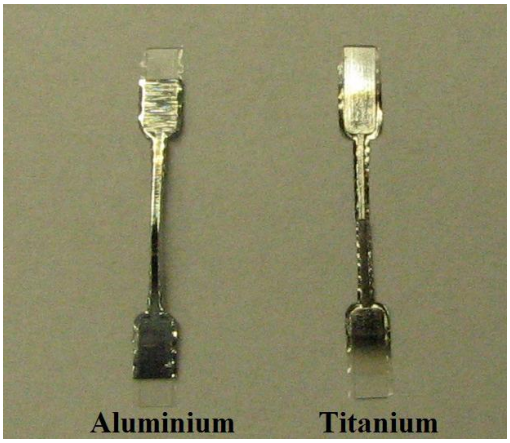


Fig.10-2 The micro injection molded weld line tensile samples with different metal coating layers

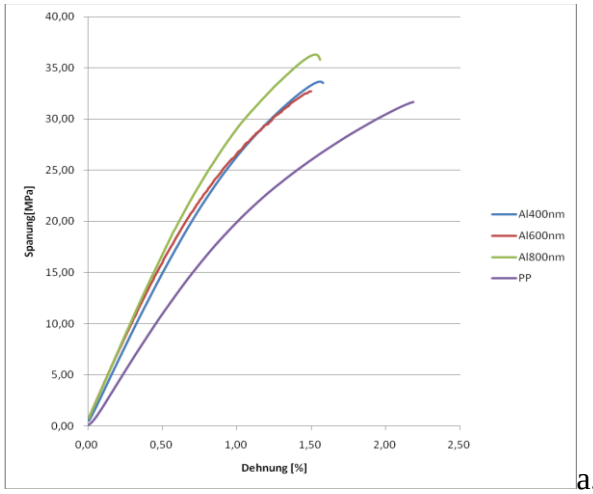
Finally, the tensile tests with the same testing configuration as Chapter 8 were implemented to characterize the weld line strength with and without metal coating layers reinforcing.

10.2 Analysis of the results

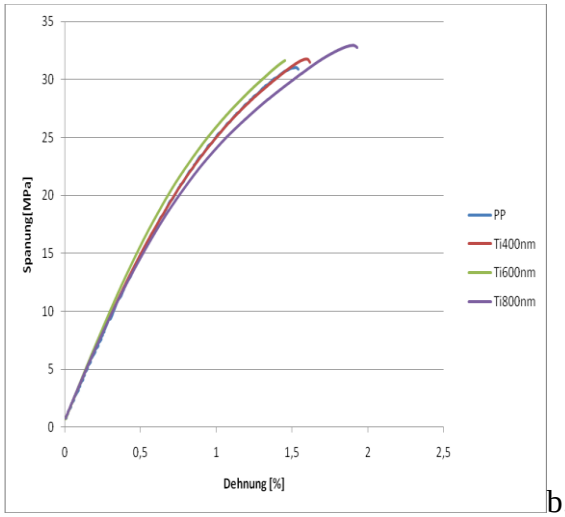
The Fig.10-3 shows the testing stress versus strain curve which demonstrates that all metal coating layers performed as enhancing effects on micro injection molded weld line strength. Aluminum coating layers improve the Elastic module of weld lines and titanium coating layers increase weld lines elongation percent of those. Additionally, due to the weld line

occurrence, the testing curve of samples without coating films show only elastic region, in contrast, the samples with metal coating films show both of elastic and plastic regions resulting from the strengthening of those coating films..

From Fig.10-4 and Fig. 10-5, it can be found that with the increasing Al and Ti coating layer thickness, the tensile strength was improved (Al layers leads to 5~13% improvement; Ti layers leads to 3% improvement). It could be explained that when the coating layers thickness is close to the V notch depth in weld line areas, the stress concentration at V notch will be decreased gradually, which results in higher weld line tensile strength. Additionally, the metal coating layer has better mechanical properties comparing with the PP and the adhering metal layers on micro tensile sample contribute to extra reinforcement during the tests. Comparison to Ti coats, Al shows better performance in general for improving strength of the weld line in micro injection molding.



a.



b.

Fig.10-3 Tensile test strain-failure curves of coated micro injection molding samples with various materials and thickness

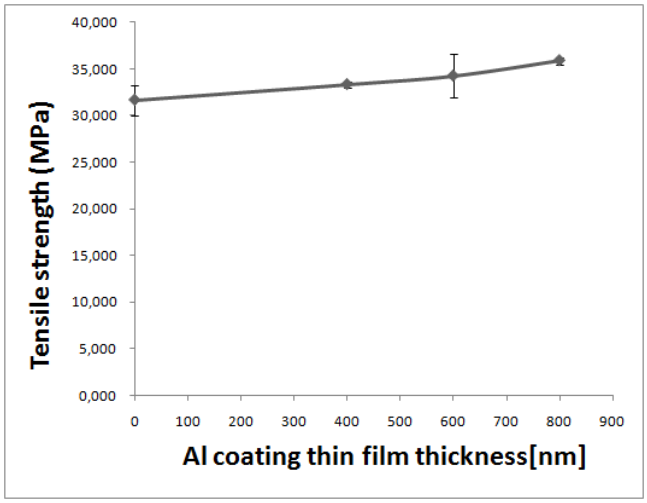


Fig.10-4 Micro injection molded weld line strength with various Al coating layer thicknesses

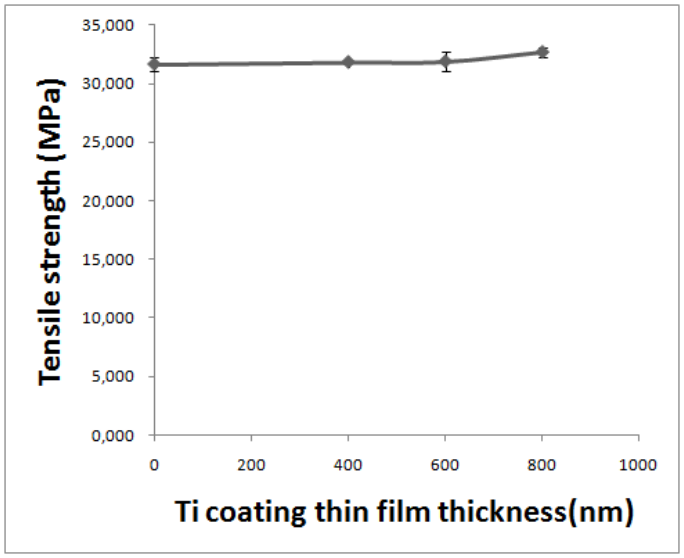


Fig.10-5 Micro injection molded weld line strength with various Ti coating layer thicknesses

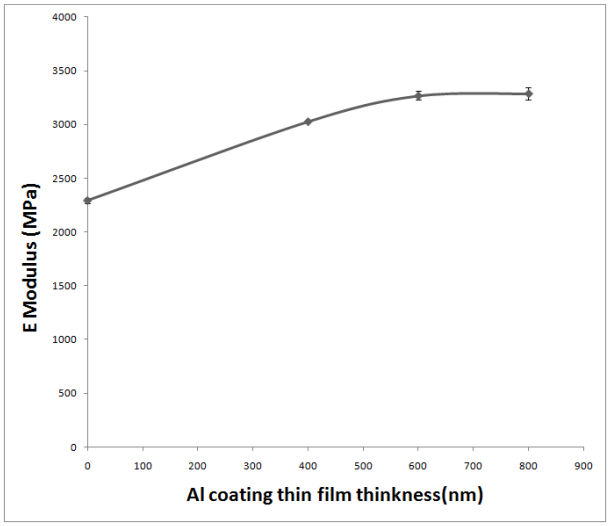


Fig.10-6 Micro injection molded weld line E module with various Al coating layer thicknesses

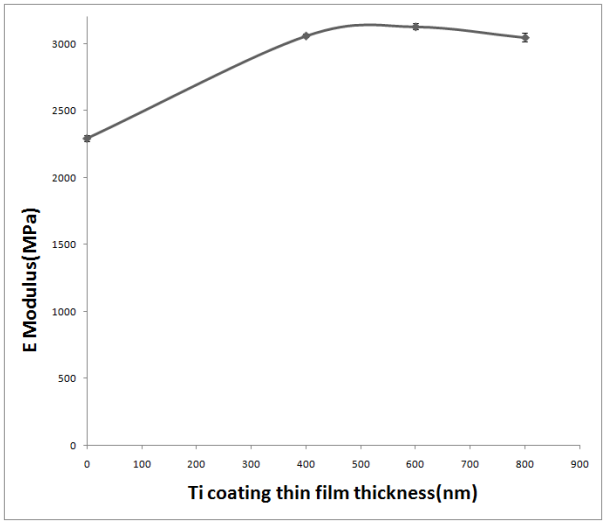
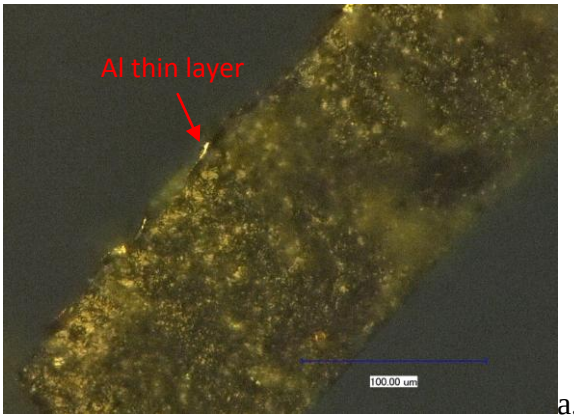
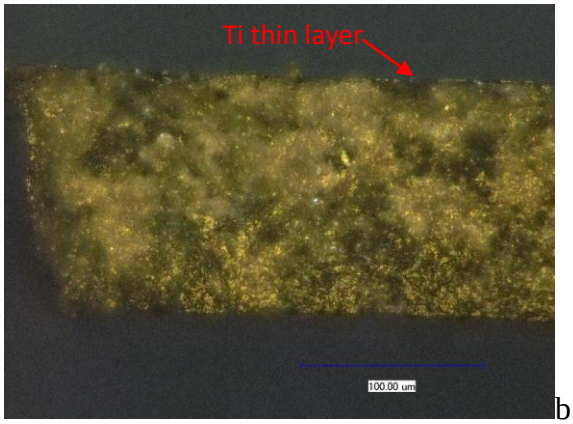


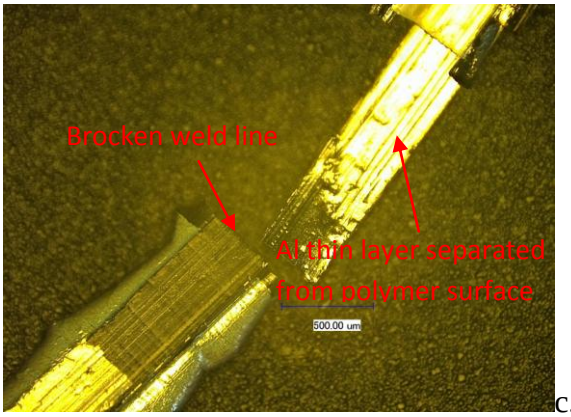
Fig.10-7 Micro injection molded weld line E module with various Ti coating layer thicknesses



a.



b.



c.

Fig.10-8 Microscope images of micro weld line tensile broken sections with different coating thickness and materials: a. Al 400nm; b. Ti 400nm; c. Al 800nm (Scale bar 100 μm)

The E module of the weld line tensile test samples combined with coating layers are also illustrated in Fig.10-6 and 10-7. With the coating layer adhesion, the E module of the micro weld line is increased. However, when the layer thickness reached 600 nm, the effect of increasing layer thickness on rising weld line E module is not obvious. The possible reason could be that with the increasing thickness of the coating layers, the adhesion force between coats and polymer samples are decreased, which will cause the separation between them. This separating behavior is harmful to load transferring and finally reduces their combining deformation resistance. Fig.10-8 shows the images of broken sections of the coated micro tensile samples with weld lines under microscopes. In Fig10-8c, the stripped 800nm Al coating layer is clearly displayed. The micro tensile sample and coating layer are broken respectively and sequentially in different moments. At a thickness of 800nm, Titanium coating thin film unexpectedly shows declined performance in adding the E modulus of micro injection molded weld line sample, which could be attributed to this reason.

In Fig. 10-9 and 10-10, the results about elongation percent of the coated weld line samples implies that Ti coating layers generally increased the plastic deforming ability of the weld line samples, since titanium specifies good flexibility. On the contrary in Fig.10-9, the Al coating layers reduced the micro weld line failure-strain rates, which is the result of its higher stiffness performance compared with polymers.

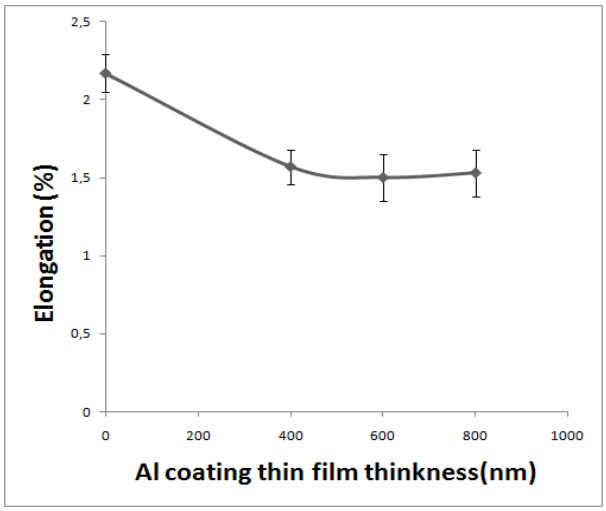


Fig.10-9 Elongation percent of micro injection molded weld line samples with various Al thin film thicknesses

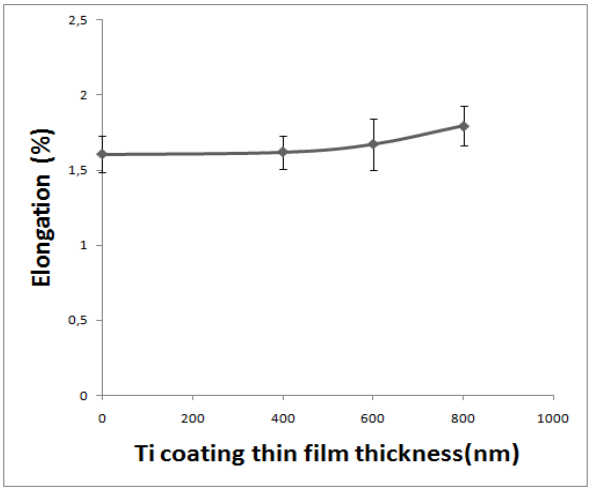
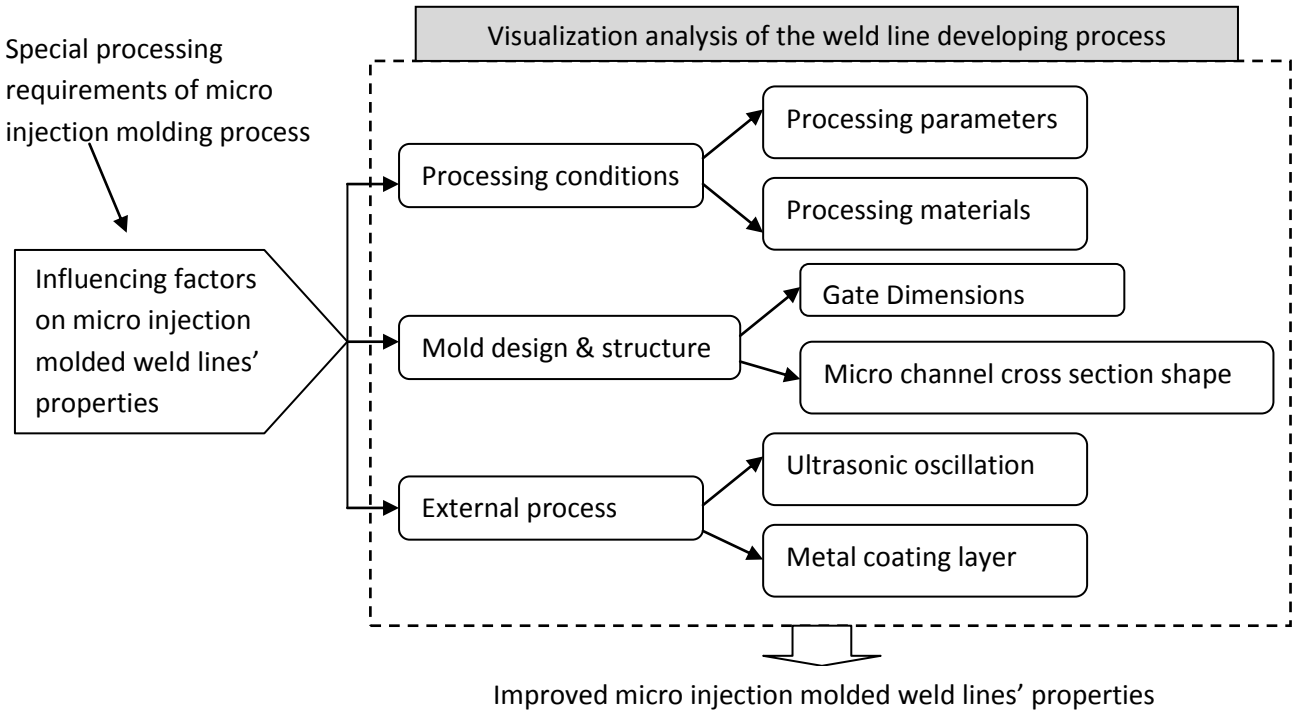


Fig.10-10 Elongation percent of micro injection molded weld line samples with various Ti thin film thicknesses

Summary

The potential functional PVD metal thin films can perform as the reinforce agent for the micro injection molded weld line as well, even with hundreds of nano meters thickness. The two kinds of coating metals, Aluminum and Titanium, enhanced not only the strength of micro injection molded weld line (Tensile strength) but also its stiffness (E modulus), because the coating thin films act as the effective valid role in releasing the stress concentration at weld line area by reducing the V notch size and transmitting the stress load to a wider area over the sample surface. However, the adhesion between the metallic PVD coating films and polymers represented the correlated influence on the enhancing performance of these coating films, especially when the thickness of film is increasing.



11 Visualization analyses for weld line developing in micro injection molding

In order to control and monitor the process of micro injection molding, many researcher use sensors for pressure and temperature to evaluate the dynamic process But the electronic sensors and transducers still have a problem due to their size, which make them hard to insert into the micro structure cavity directly. Regarding the requirements of fine features and dimensions, these monitoring methods are not possible. Additionally, the sensor data acquisition system only can provide the indirect information how the parameters vary during process, but not the real filling and flow behavior of the polymer melts in the micro cavity. Therefore, the method which can supply more direct observation for polymer melts flow behavior study is desired to develop. The visualizing method with a glass insert mold was applied and satisfied with the requirement quite well.

11.1 Experimental principle and setup

11.1.1 Principle

In order to realize the visualizing function, a special glass insert mold is designed for performing the direct visual analysis for melt flow phenomena in micro injection molding. Through the high speed camera the whole polymer filling and weld line forming process were recorded. After the image processing, melt flow behavior and the cavity filling time with various processing conditions were obtained and analyzed.

11.1.2 Visualization mold design and realization

A visualization mold with glass insert was designed and constructed. Through the initial test and trial- mold, the structure and strength of glass insert were improved and optimized based on the previous design [80], shown as Fig. 11-1.

In the modified glass insert mold, structure of the glass insert was modified as a whole block shaping similar as a cube, which is helpful to improve the enduring pressure of the glass part and avoid its broking during injection processing. A steel frame is used as the support for the glass insert. Its dimension is a little bigger than the slot which is its assembly position. It was assembled with the mold when the mold was heat up to 150 °C then cooled them down, which can make sure the support frame will not be lose when the mold is heated up to high temperature by the variothermal unit in mold. Fig.11-2 presented the structure and assembly position of the glass part.

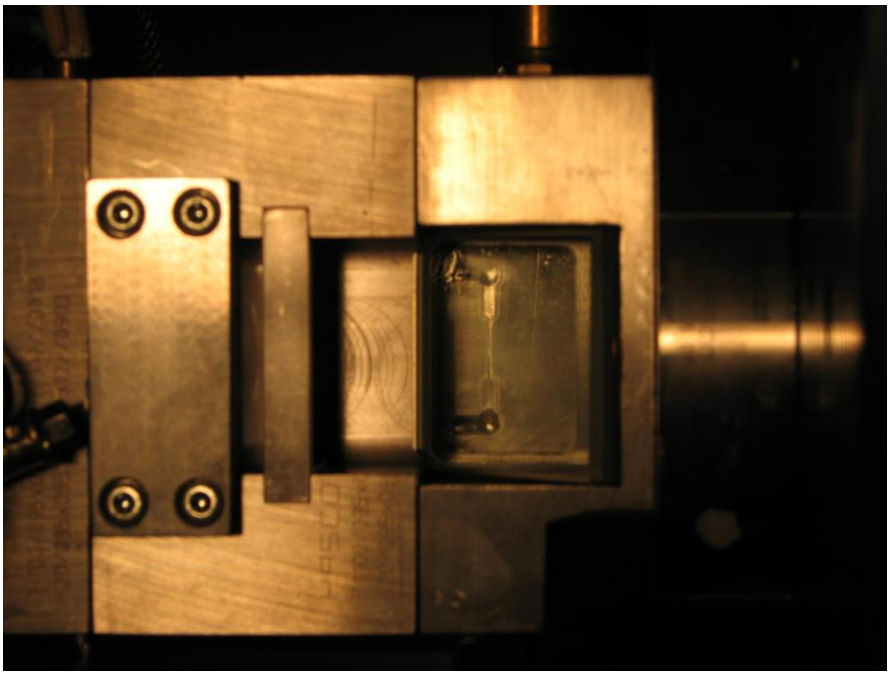


Fig.11-1 Glass insert mold, real appearance of stationary mold side

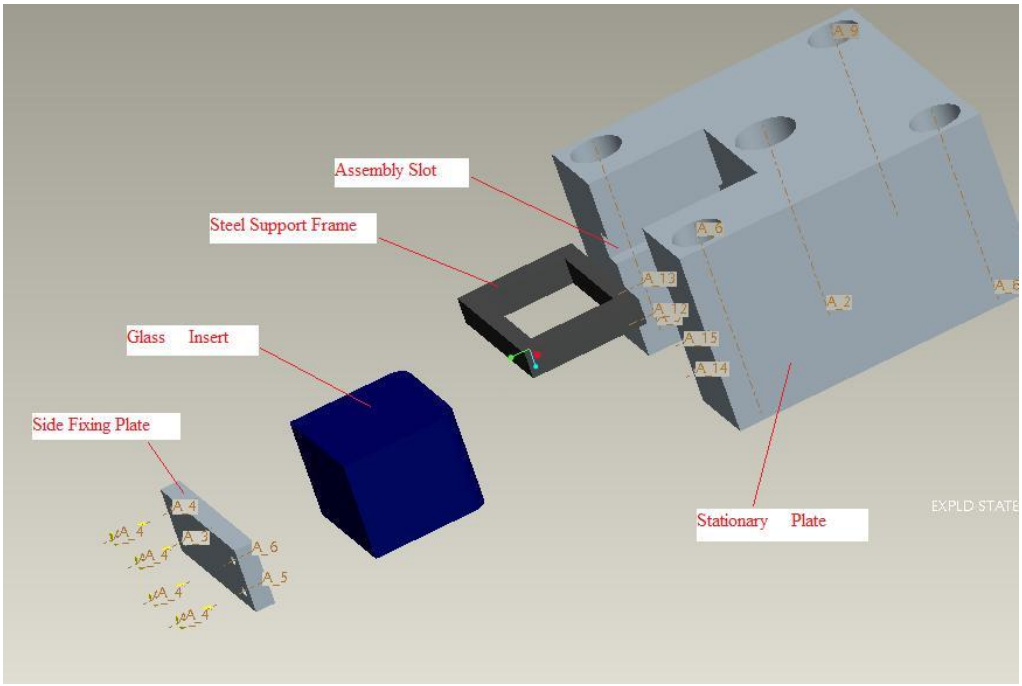


Fig.11-2 3D Explosion Drawing for moving side of the glass inert mold

The recording system for weld line developing is a high speed camera with video/image processing software (HSC 1000P), show in Fig. 11-3. The recording speed of the high speed camera was set as 923 fps (picture size: 1024×768 Pixel).

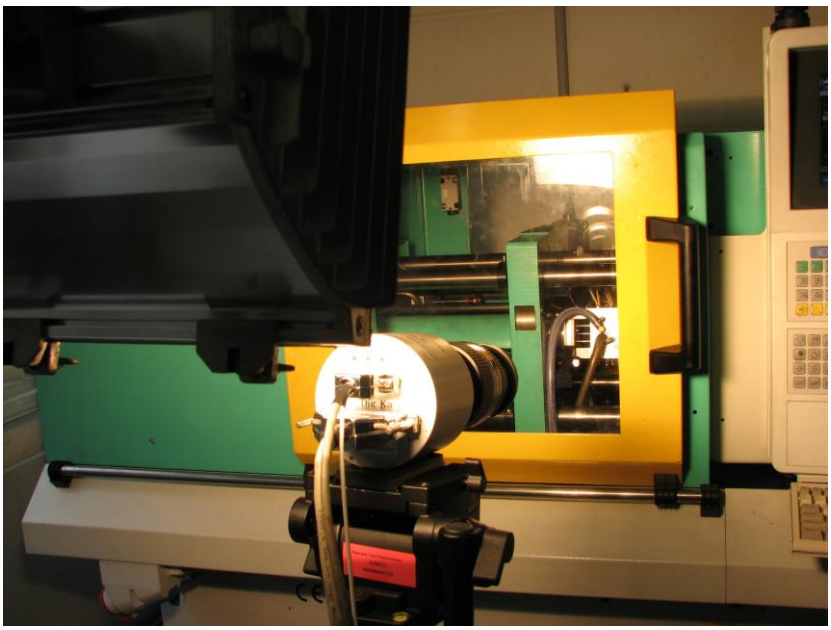


Fig.11-3 High speed camera used as the recording system

11.2 Experiment Results and Analysis

The objective molding part was the micro tensile part, which is same as the part applied in Chapter 5. According to the processing parameter listed in Table 11-1, the experiments were executed. Weld line development processes were filmed by the high speed camera, in order to investigate how the processing conditions influence the melt flow behavior in micro injection molding.

The recording software for high speed camera integrated the function for marking and calculating the duration time when the melt is flowing through the whole micro tensile sample cavity (t_w) and when the melt is filling the middle micro channel of the micro tensile part (t_m), the definition of the cavity parts is shown in Fig11-4. Fig. 11-5 presents the melt flow front advances at different moments with 25 MPa injection pressure, 20cm^3/s injection speed, 240°C melt temperature and 120°C mold temperature.

Table11-1 Experimental processing parameters

Melt temperature (°C)	Injection speed (cm^3/s)	Injection pressure (MPa)	Mold temperature (°C)
240	15	40	120
	20	25	120
	20	30	120
	20	40	120
	20	30	135

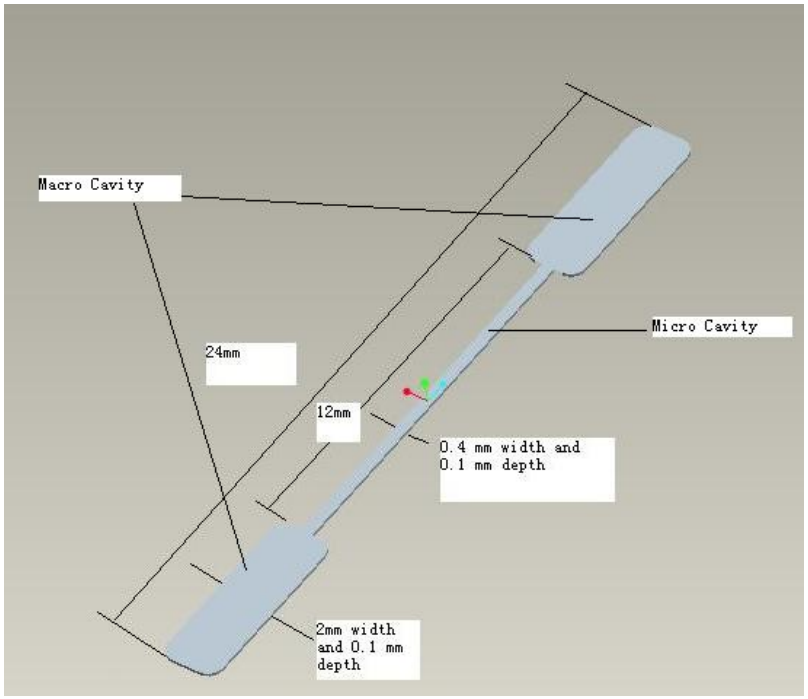
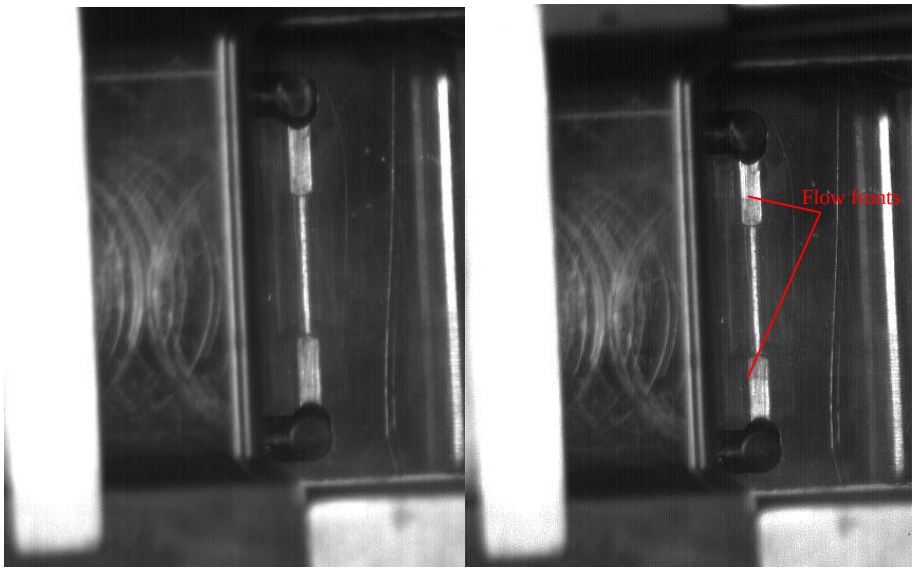
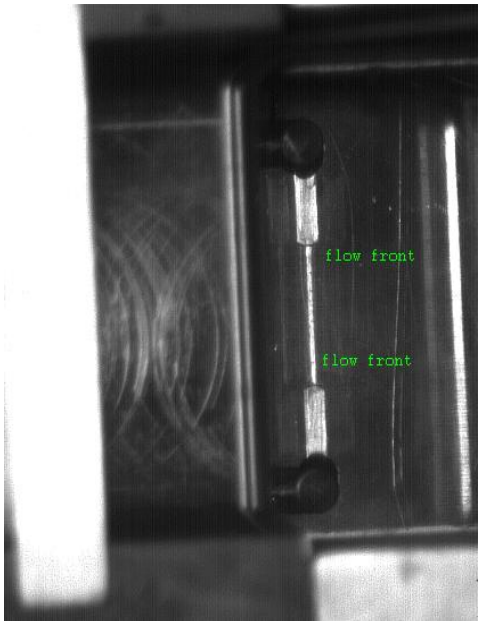


Fig.11-4 The definition of the cavities' position in the tensile part

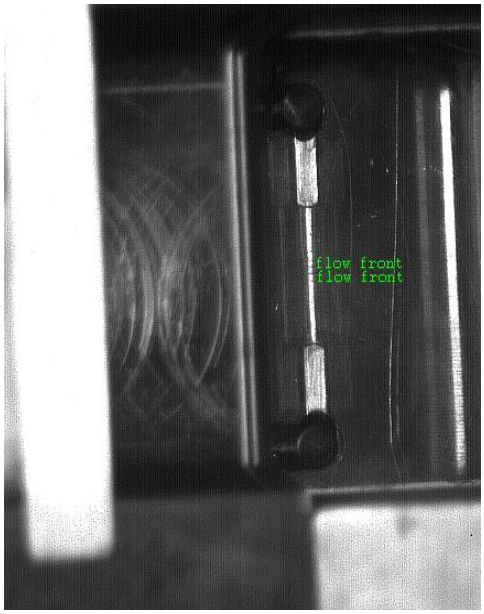


t = 0s t = 0.00758s



t=0.02166s

t=0.03466s



t=0.07581s

Fig.11-5 Melt flow front advances at different moments with 25 MPa injection pressure, 20cm3/s injection speed, 240 melt temperature and 120°C mold temperature

The experimental processes were recorded and compared at different injection pressure (25MPa, 30MPa, 40MPa), injection speed (15cm^3/s, 20cm^3/s) and mold temperature (120°C, 135°C). The results are plotted in Fig.11-6-Fig.11-8, and the filling time unit is ms (micro second).

Fig.11-6 shows how injection pressure affects the filling time of melts through the whole cavity, micro cavity and relative macro cavity respectively. According to the results, when the other processing parameters are constant, the injection pressure dramatically influenced the time that melts fill with cavity. Filling time for the whole cavity and micro cavity are quite shorter at higher injection pressure. In contrast, the injection pressure has hardly effect on the filling time for the relative macro cavity. Therefore, one can conclude that the main reason for influencing the filling time for the whole cavity is the melt flow behavior in the micro cavity. The higher injection pressure contributes to faster flowing in micro channel.

The correlation between injection speed and filling time is also investigated. In Fig.11-7, with the same melt temperature and mold temperature. At 40 MPa injection pressure, the filling time related to higher injection speed (20 cm^3/s) is much shorter than the one in lower injection speed (15 cm^3/s). So based on the results, as a matter of fact, in micro injection molding, higher injection pressure and injection speed really result in faster and easy filling in micro scale cavity.

Additionally, the mold temperature is also varied for the purpose of finding the relation between mold temperatures and melt flow behavior. Fig.11-8 shows a very clear fact that higher mold temperature (135 °C) reflects on shorter filling time, especially for the micro cavity filling phase. In the plot, the improvement for filling time throughout relative macro cavity hardly can be recognized. In contrast, the filling time throughout micro cavity is promoted dramatically.

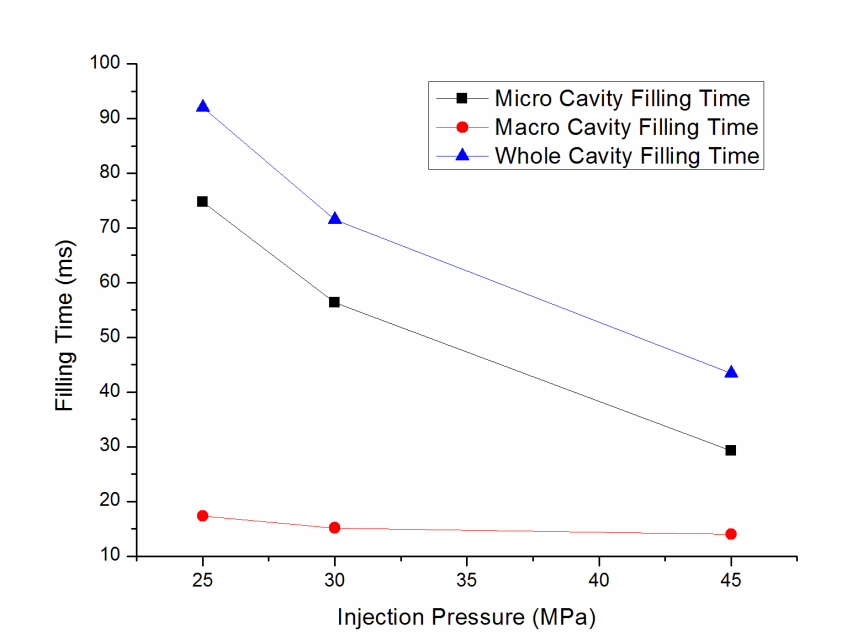


Fig.11-6 Filling time for different parts of micro tensile part at 2 injection pressures, which are carried out in 20 cm3/s injection speed, 240°C melt temperature 120°C mold temperature

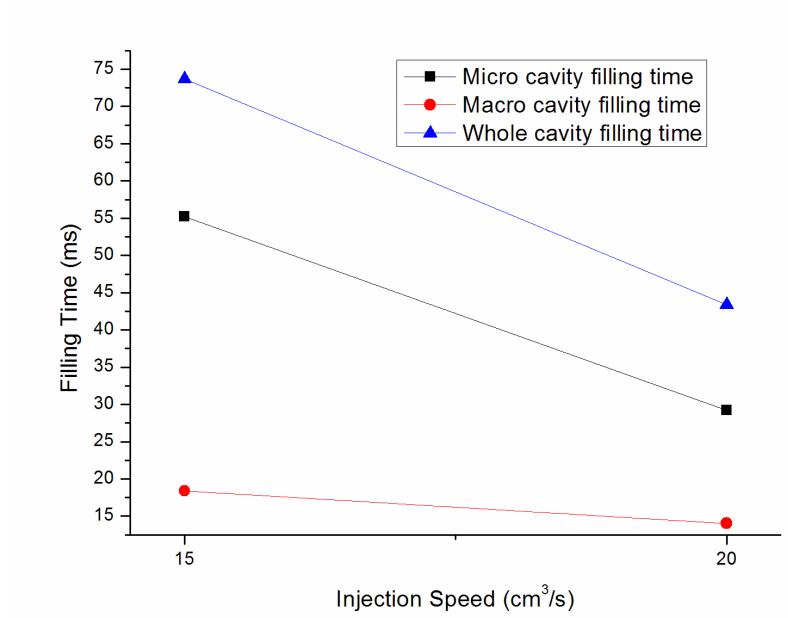


Fig.11-7 Filling time for different parts of micro tensile part at 2 injection speed, which are carried out in 40 MPa injection pressure, 240°C melt temperature 120°C mold temperature

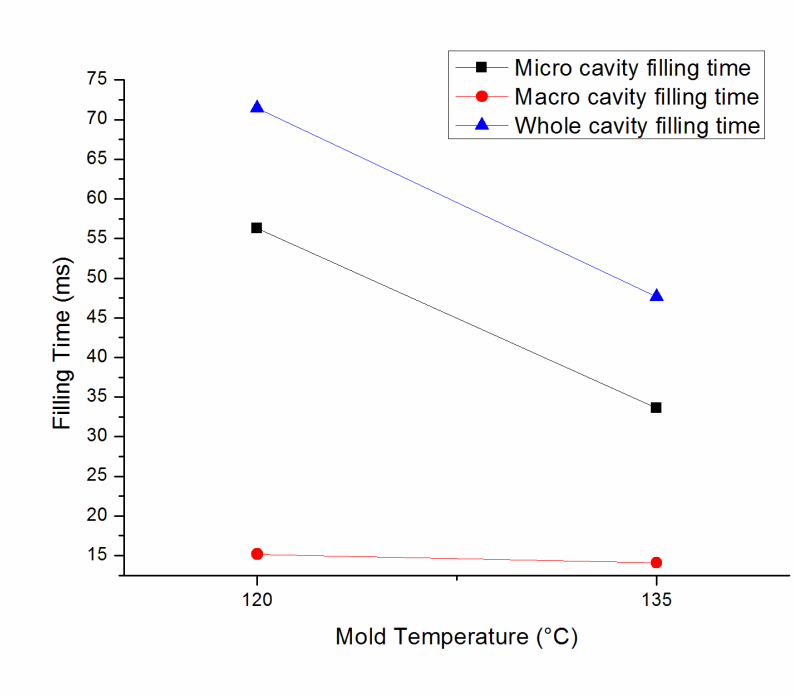


Fig.11-8 Filling time for different parts of micro tensile part at 2 mold temperature, which are carried out in 30MPa injection pressure, 240°C melt temperature, 20 cm3/s injection speed

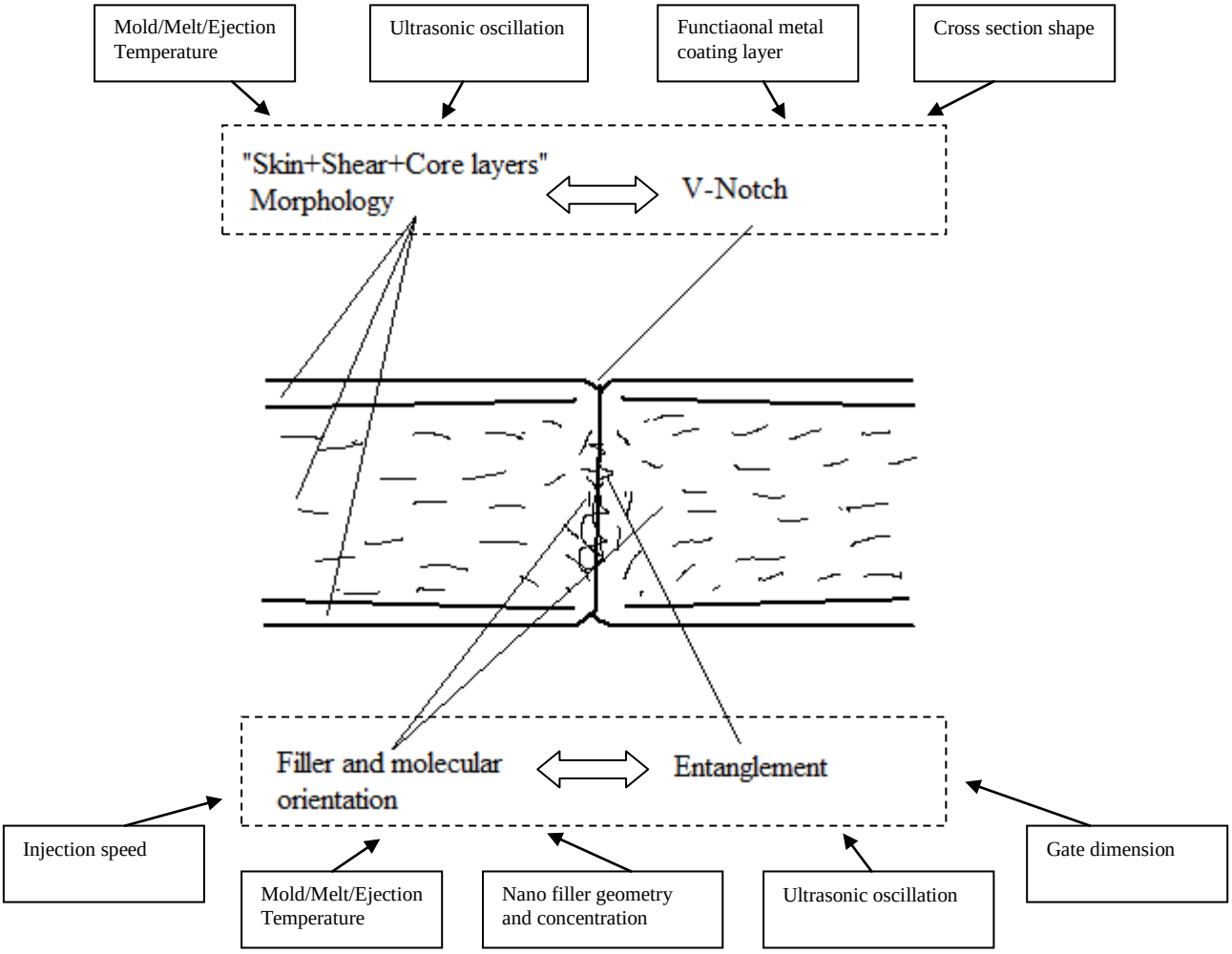
Summary

In this chapter, the melts flow visualization analysis in micro injection molding was carried out by a visualizing mold. The glass insert mold with visualizing function was designed, constructed and assembled. Some conclusions according to the experimental results can be drawn as follows:

1. At 20cm^3/s injection speed, the effect of injection pressure on the flowing behavior was regard as strong. Higher injection pressure conduces faster filling phase. However, this effect is only suitable for the micro cavity filling not for macro cavity;

2. With the constant melt temperature and mold temperature, injection molding speed is able to do a good performance for improving the filling time of micro cavity, while as for macro cavity filling, the effect of injection speed on filling time is not obvious;

3. Mold temperature is also doing a positive function for promoting the filling time to shorter, since the higher mold temperature can make the melt frozen slower and the viscosity lower.



12 Conclusions and Perspective

12.1 Conclusions

Heading to reveal the influencing factors related to micro injection molded weld line strength, various polymer materials, injection moulds and characteristic methods were applied in the presented works. 3 classified ranges of effecting factors on weld line strength in micro injection molding process were defined and studied, which are namely processing conditions, mould design & structure and external process.

In processing conditions range, there are 2 factors are listed: the correlation between micro injection molding process parameters and weld line strength, as well as the effects of nano filler geometry and concentration on weld line strength.

For the former, the results revealed that in micro injection molding, mold temperature is the most important parameter for weld line strength, melt temperature is following; Injection speed and ejection temperature are located in 3rd and 4th place; Not like the fact known in traditional injection molding, injection pressure and packing pressure are not playing significant role in weld line enhancing. The optimizing levels of all process parameters were obtained based on the Taguchi experimental design and analysis. An experience prediction model for weld line strength was achieved by multi regression method.

For the latter, nano carbon fibers and TiO2 particles are compounded with Polypropylene in various weight contents (10%, 20%, 30% and 35%) and processed by micro injection molding for preparing micro tensile samples with weld lines. The tensile test results show the fact that the weld line strength of nano filled polymer system is reduced, except in the case of 10% carbon nano fibers filled PP; The strains of the nano composites in weld line area are smaller than neat PP, and when the loading is lower than 20%, the weld line of nano CNF and hybrid nano CNF/TiO_2 composites have a comtribution to larger tensile strain than nano TiO_2 composites; but in the range higher than 20%, the nano TiO_2/PP system responses to the higher strain-to-failure value of weld line; Carbon nano fibers dominate the E modulus and tensile strength of the weld line for all nano composites. CNF and hybrid CNF/TiO_2 composites always lead to higher E modulus and tensile strength than TiO_2 composites for micro injection molded weld line. With increasing contents of nano filler, in CNF and Hybrid CNF/TiO_2 composites, the E modulus and tensile strength of weld line are decreased; in TiO_2 composites, 10 weight % is a threshold value, lower than it the E modulus and tensile strength of weld line are decreased, but higher than it, they are increased also.

In mould design & structure range, influences of micro channels' cross section shape and mould gate dimensions with weld line strength in micro injection molding process were investigated. Regarding to effects of micro channel cross section shape, the weld line specimens were formed by injection molding and characterized with tensile tests. Micro injection molded weld line specimen with 3 different cross section shapes were analyzed. The weld line strength was found to relate to the ratio of cross section perimeter to area, named as *a*. The cross section with higher a has better performance in adding a value of weld line strength. Concerning with the influencing of gate dimensions, the results for PP show that with the changing of injection pressure and mold temperature, Gate Nr.3(1.0×0.05×0.5mm, width, depth, length) is corresponding to the strongest weld strength, the following is Gate Nr.2(1.0×0.1×0.5mm, width, depth, length); Gate Nr.4 (0.5×0.1×0.5mm, width, depth, length) and Gate Nr.1(1.5×0.1×0.5mm, width, depth, length) are in the end. The difference between

them is not obvious. For HDPE, results presents that Gate Nr.3 always gives the best weld line strength whatever the processing parameters are, Gate Nr.4 is following and then is Gate Nr.2. There are always middle optimal values for processing parameters leading to strongest weld line strength, when injection pressure is 80MPa, injection speed is 90 cm3/s, melt temperature is 200°C and Mold Temperature is 130 °C. Higher and lower processing parameters result in reduced weld line strength.

In external process range, the reinforcing mechanisms research of ultrasonic oscillation and metal coating layer for weld line strength in micro scale were carried out. One ultrasonic generator with sonotrod was integrated in the micro injection mould. During the micro injection molded weld line samples preparation, 3 output power levels (400W, 600W and 800W) and 2 inducing mode (Mode1. the oscillation is induced from injecting moment to ejection moment; Mode2. the oscillation is induced from injecting moment to packing procedure finishing) were set. The fact was found that ultrasonic oscillation has obvious influence on the weld line strength in micro injection molding process; Mode 2 always has better performance than Mode 1 for reinforcing the weld line strength; and when output power is 400W the weld line strength is the highest.

As for the metal coating layer effects, the micro tensile samples with weld lines were coated by physical vapor deposition process respectively with Titanium and Aluminum in 3 different thicknesses (400nm, 600nm and 800nm). Throughout the tensile measurement, the enhancing of the coating layer on weld line strength was observed. For both coating materials, thicker layer results in better improvement for the micro weld line strength.

Last but not least, it is worth mentioning that a visual mould was constructed in order to direct observe the polymer melts micro flow behavior and weld line forming. Based on the visual images and videos gained, it could be demonstrated that in micro injection molding process, the cavity filling time is majorly occupied by micro structure's filling. The injection pressure put an obvious effect on the filling speed through micro cavity. Injection speed can shorten the filling time dramatically also. Higher mold temperature brings positive influence with the flowing speed.

12.2 Perspective

12.2.1 Issues need to improve in future

- The resolution of the high speed camera and the light source for the camera are not good enough which the obstacle to get more precise and clear pictures and films for the visualizing analysis of weld line development.

- The mold material needs to be improved in the aspect of thermal stability, since the variotherm system has a strict requirement about it. Otherwise, the work life and precision of the mold will decrease dramatically after hundreds of shots.

- Morphology investigation samples prepared by microtome should be more precise and the special holding tool for the micro samples used for microtome remain to be developed for better cutting precision

- The allowed minimum weight of the test sample for DSC should be improved. Normally the DSC sample should be heavier than 10 mg, which gives correct results. However the whole micro injection molded part in this project is less than 3 mg. When the crystal situation in different part of the micro part need to investigated, the precision of 10 mg for measuring sample weight is definitely inadequate.

12.2.2 Further research topics in future

Since Weld lines are formed during mold filling whenever two separated melt streams recombine and there always is a V-notch formed in the weld line area, which have to be handled similar to a crack. When extra energy from outside can minimize, fill, and even erase this "V-Notch", the weld line's strength would be able to be reinforced significantly for many applications. Based on the results and experiences from the previous project, the advanced method which constitutes with **precise local variotherm** and **self healing technologies** is believed to be capable of reaching these special requirements and challenging aims.

In addition, the topics related to the effect of injection mould material and micro cavity surface roughness on weld line strength would be also very interesting and demand more investigation, since the mould material and surface quality are associated with the melts flow behavior particularly in micro scale injection molding (in this case surface tension effect and wall slip are getting important).

Furthermore, with various micro injection molding processing conditions, crystallinity distribution and measurement in different sectors of micro parts, especially in the area around weld line would be also a potential key issues which is close to the micro weld line mechanical properties.

List of References

[1] Madou M. J., Fundamentals of Microfabrication, CRC Press, Boca Raton, 1997.

[2] Madou M. J., Fundamentals of Microfabrication: The Science of Miniaturization, 2nd ed. CRC Press, Boca Raton, FL, 2002.

[3] Yu L. Y., Experimental and numerical analysis of injection molding with micro features, PhD Dissertation, Ohio State University, Ohio, U.S.A, 2004

[4] Wilson K., Molnar P. and Hickman J., Integration of functional myotubes with a Bio-MEMS device for non-invasive interrogation, Lab on Chip, 2007, 7: 920-922

[5] Spatz Joachim P., Bio-MEMS: Building up micromuscles, Nature Materials 4, 2005,4:115-116

[6] Pal, P., Sato, K., Silicon microfluidic channels and microstructures in single photolithography step, Design, Test, Integration & Packaging of MEMS/MOEMS, 2009. MEMS/MOEMS '09. Symposium, 1-4,April,Rome, 2009:419-423

[7] Heckele M and Schomburg WK, Review on micro molding of thermoplastic polymers, J. Micromech. Microeng.2004,14: 1-14

[8] Michaeli,W Roalla. A., Spennemann A., Ziegmann C.. Mikrostrukturierte Formteile aus Kunststoff gestalten, F&M Feinwerktechnik, Mikrotechnik, Mikroelektronik, 1998,9:642-645.

[9] Ansel Y., Schmitz F., Kunz S., Gruber H.P. and Popovic G.. Development of tools for handling and assembling microcomponents. Journal of Micromechanics and Microengineering. 2002,12: 430-437

[10] Piotter V., Bauer W., Benzler T., Emde A.. Injection miolding of components for Microsystems, Microsystems technologies, 2001,7: 99-102

[11] Eberle H.. Micro-injection moulding technology, Kunststoffe Plastic Eourope, 1998:1344-1346

[12] Klein H., J.Schulz, A.Spennemann, C.Ziegmann. Machine and process develop -ment for micro engineering, Block 1, 20. IKV-Kolloquium Aachen, 2000.

[13] Wu C. H., Liang W. J., Effects of geometry and injection-molding parameters on weld line strength, Polymer Engineering and Science, 2005:1022-1030

[14] Hanemann T, Heckele M and Piotter V. 2000 Current status of micromolding technology. Polym. News, 25: 224–229

[15] Michaeli W. , Spennemann A. , Gärtner R. . New plastification concepts for micro injection moulding, Microsystem Technologies (2002)8: 55–57

[16] Xie L, Visualization analysis of micro injection molding weld line development, 10 year PuK Syposium, Oct. 2008.

[17] Giboz J., Copponnex T. and M´el´e P.. Microinjection molding of thermoplastic polymers: a review, J. Micromech. Microeng. (2007)17:96–109

[18] Heckele M, Schomburg WK. Review on micro molding of thermoplastic polymers, J. Micromech. Microeng. (2004) 14: 1–14

[19] Becker H., Gärtner C.. Polymer microfabrication technologies for microfluidic systems, Anal Bioanal Chem (2008) 390:89–111

[20] Sha B. C., Dimov S., Griffiths C., Packianather M. S.. Micro-injection moulding: Factors affecting the achievable aspect ratios, Int J Adv Manuf Technol. (2007)33: 147-156

[21] Sabu T. and Yang W. M.. Edited, Advances in polymer processing---From macro to nano scales, Woodhead Publishing in Materials

[22] Piotter V. , Hanemann T. , Ruprecht R. and Haußelt J. , Injection molding and related techniques for fabrication of microstructures, Microsystem Technology, (1997)3:129-133

[23] http://www.battenfeld-imt.com/en/anwendungstechnik.html

[24] http://www.ormocer.de/EN/mikrosystemtechnik/index.jsp

[25] http://me.kaist.ac.kr/english/

[26] http://www.nmp.kit.edu/

[27] Martyn M T, Whiteside B, Coates P D, Allan P S,Greenway G and Hornsby P 2003 Micromoulding: consideration of processing effects on medical materials SPE ANTEC Proc.

[28] Mekaru H, Yamada T, Yan S and Hattori T 2004 Microfabrication by hot embossing and injection molding at LASTI Microsyst. Technol. (2004)10: 682–688

[29] Schift H, David C, Gabriel M, Gobrecht J, Heyderman L J, Kaiser W, Koeppel S and Scandella L 2000 Nanoreplication in polymers using hot embossing and injection molding, Microelectron. Eng. 53: 171–174

[30] Yao D. and Kim B. Injection molding high aspect ratio microfeatures, J. Injection Molding Technol. (2002)6: 11–17

[31] Liou A. C. and Chen R. H. Injection molding of polymer micro- and sub-micron structures with high aspect ratios Int. J. Adv. Manuf. Technol. (2006) 28: 1097–1103

[32] Despa M. S., Kelly K. W. and Collier J. R. 1999 Injection molding of polymeric LIGA HARMS Microsyst. Technol. 660–666

[33] Gobrecht J, Schift H, David C, Kaiser W, D'Amore A, Simoneta D and Scandella L. Injection molded plastic chip for calibration of scanning probe microscopes PTB Berichte PTB-F-39 (2000): 1–7

[34] Piotter V., Mueller K., Plewa K., Ruprecht R. and Hausselt J. 2002 Performance and simulation of thermoplastic microinjection molding, Microsyst. Technol. 8 387–90

[35] Kelly A. L., Woodhead M and Coates P D 2005 Comparison of injection molding machine performance Polym. Eng. Sci. 45 857–65

[36] Bibber D. M. 2004 Micro molding challenges SPE ANTEC Technical Papers 3703-11

[37] Whiteside B., Spares R. et al. Combined flow visualization and ultrasonic for characterization of the micro moulding process, PPS 24, 2008, June 15-19, Salerno, Italy.

[38] Whiteside B.R., Martyn M.T., Coates P.D., Greenway G., Allen P., Hornsby P., Plastics, Rubber and Composites, 32, no. 6, pp. 231-239, 2003.

[39] http://www.battenfeld-imt.com/en/maschinen/baureihen/micro.html

[40] http://www.battenfeld-imt.com/fileadmin/user_pdf/maschinen/baureihen/micro/msystem 50_en.pdf

[41] Kupka R., Bouamrane F. and Megtert S. . Microfabrication of massive parallel micromirror-lenses by X-ray LIGA technique: recent advances and prospects, Microsystem technologies,(2008)10:22-28

[42] Ron A. Lawes. A traceable fabrication process for X-ray LIGA: easier access for industry, International journal of nanomanufacturing (2008) 2,(6):572 - 582

[43] Luo Y., Wang X. D., Liu C., Lou Z. F., Chu D. N. and Yu D. H. Swelling of SU-8 structure in Ni mold fabrication by UV-LIGA technique, microsystem technologies,(2005)11, (12):1272-1275

[44] Munnik F., Benninger F., Mikhailov S., Bertsch A., Renaud P., Lorenz H., Gmuer M.. High aspect ratio, 3D structuring of photoresist materials by ion beam LIGA, Microelectronic Engineering (2003)67-68: 96–103

[45] http://ankaweb.fzk.de/_cms/_release/methods_at_anka/microsystems_technology.php

[46] Chiffre De, Kunzmann L., Peggs H., Lucca G.N.. Surfaces in precision engineering, microengineering and nanotechnology, 2003Annals of the CIRP, 52/2: 561-577.

[47] Bang Y. B., Lee K. M and Oh S. 5-axis micro milling machine for machining micro parts, The International Journal of Advanced Manufacturing Technology,(2005)25:888-894

[48] Baptista R, Antune Simões JF. Three and five axis milling of sculptured surface. J Mater Process Technol (2000) 103:398–403

[49] Arai Y., Asai T., Ferdous S. and Gao W., 3D Profile Measurement of Nanometer Cutting Edges of Single-Point Diamond Tools for Ultra-Precision Machining, Advanced Materials Research (2009)69-70:138-142

[50] Fang F Z, Venkatesh V C, Zhang G X. Diamond turning of soft semiconductors to obtain nanometric mirror surfaces. Int. J. Adv. Manuf. Technol. 2002 (19): 637–641

[51] Yan J.W., Tamaki J., Syoji K. and Kuriyagawa T. Single-point diamond turning of CaF 2 for nanometric surface, Int. J. Adv. Manuf. Technol. 2004 (24): 640–646

[52] Allen, D. M., Lechebeb, A., (1996), "Micro electro-discharge machining of ink jet nozzles: optimum selection of material and machining parameters", Journal of Materials Processing Technology. 58:53–66

[53] Liu, H. S., Yan B. H., Chen, C. L., Huang, F. Y., (2006), "Application of micro-EDM combined with high-frequency dither grinding to micro-hole machining", International Journal of Machine Tools & Manufacture 46 80–87.

[54] Cho, Y.R.; Oh, J.Y.; Kim, H.S.; Jeong, H.S. Micro-Etching Technology Of High Aspect Ratio Framework For Electronic Devices Microprocesses and Nanotechnology Conference, 1998 International , 13-16 Jul 1998 :221 – 222

[55] Kassing R. and Rangelow I. W. Etching processes for High Aspect Ratio Micro Systems Technology (HARMST), microsystem technologies,(1996)3, (1): 20-27

[56] Hu H., Ricken R., Sohler W., and Wehrspohn R. B., "Lithium Niobate Ridge Waveguides Fabricated by Wet Etching", IEEE Photon. Technol. Lett., (2007) 19:417–419

[57] Bellouard Y., Said A., Dugan M., and Bado P.. Fabrication of high-aspect ratio, micro-fluidic channels and tunnels using femtosecond laser pulses and chemical etching, Optics Express, (2004) 12,(10): 2120-2129 doi:10.1364/OPEX.12.002120

[58] Ho C.M.. Micro-electro-mechanical-systems(MEMS) and Fluid flows, Annual Review of Fluid Mechanics, (1998) 30: 579-612 doi:10.1146/ annurev.fluid.30.1.579

[59] Arnold J., Dasbach U., Ehrfeld W., Hesch K. and Löwe H.. Combination of excimer laser micromachining and replication processes suited for large scale production, Applied Surface Science, (1995)85: 251-258

[60] Klank H., Kutter J. P. and Geschke O.. CO2-laser micromachining and back-end processing for rapid production of PMMA-based microfluidic systems, Lab on a Chip (2002) 2: 242–246

[61] McCreedy T., Rapid prototyping of glass and PDMS microstructures for micro total analytical systems and micro chemical reactors by microfabrication in the general laboratory, Analytica Chimica Acta, (2001) 427,(1), Pages: 39-43

[62] Li X.C., Choi H.S. and Yang Y.. Micro rapid prototyping system for micro components, Thin Solid Films,(2002)420-421:515-523

[63] Hawkeye M., Brett Michael J.. Glancing angle deposition: Fabrication, properties, and applications of micro- and nanostructured thin films, J. Vac. Sci. Technol A, (2007)25,(5):1317-1335

[64] Takahata K., Shibaike N. and Guckel H. . High-aspect-ratio WC-Co microstructure produced by the combination of LIGA and micro-EDM, microsystem technologies,(2000)6, (5):175-178

[65] Bertsch A., Lorenz H. and Renaud P., 3D microfabrication by combining microstereolithography and thick resist UV lithography, Sensors and Actuators A: Physical, (1999)17:14-23

[66] Quake S. R., Scherer A., From Micro- to Nanofabrication with Soft Materials, Science, (2000)290,(5496): 1536 – 1540

[67] Malek C. K., Saile V.. Applications of LIGA technology to precision manufacturing of high-aspect-ratio micro-components and -systems: a review, Microelectronics Journal,(2004)35,(2):131-143

[68] Boetter H. etal. New thermoelectric components using microsystem technologies, Journal of microelectromechanical systems, (2004)13,(4):414-420

[69] Kim B.H. and Suh N.P., Polym. Plast. Technol. Eng., 25, 73(1986).

[70] Jansen K.M.B. and Flaman A.A.M., Polym. Eng. Sci., 34, 894(1994).

[71] Yao D. and Kim B., Polym. Eng. Sci., 42, 2471 (2002).

[72] Xu X.R., Sachs E., and Allen S., Polym. Eng. Sci., 41, 1265 (2001).

[73] Wada A., Tazaki K., Tahara T., Suzuki H., and Mizutani Y., U.S. Patent 4,340,551 (1982).

[74] Brown G.H., Theory and Application of Radio-Frequency Heating, D. Van Nostrand Company, New York (1947).

[75] Michaeli W. and Spennemann A.. Kunststoffe Plast. Europe, 90(9), 16, 2000.

[76] Benzler T., Piotter V., Hanemann T., Mueller K., and Norajitra P., SPIE, 3874, 53 (1999).

[77] Schinkothe W. and Walther T., Kunststoffe Plast. Europe,90(5), 17, 2000.

[78] Weber L. and Ehrfeld W., Kunststoffe Plast. Europe, 89(10),192, 1999.

[79] Fu G. , Loh N. H. , Tor S. B. , Tay B. Y. , Y. Murakoshi and R. Maeda. A variotherm mold for micro metal injection molding, Microsyst Technol, (2005)11:1267-1271

[80] Xie,L., Ziegmann G. A visual mold with variotherm system for weld line study in micro injection molding，Microsystem Technologies, 14,(2008),6, 809-814.

[81] Xie L., Ziegmann G., Visualizing Analysis for Weld Line Forming in Micro Injection Molding by Experiment Method, Microsystem Technologies.2009,15,6:913-917

[82] Xie L., Ziegmann G. et al., Effect of micro tensile sample's cross section shape on the strength of weld line in micro injection molding process, Microsystem Technologies. 2009,15,7:1031-1037

[83] Xie L, Ziegmann G., Influence of processing parameters on micro injection molded weld line mechanical properties of PP(Polypropylene), Microsystem Technologies. 2009,15,9:1427-1435

[84] Xie L., Ziegmann G., Effect of Gate Dimension on Micro Injected Weld Line Strength with Polypropylene (PP) and High Density Polyethylene (HDPE). International Journal of Advanced Manufacture technology. DOI:10.1007/s00170-009-2276-4

[85] Xie L, Ziegmann G., Jiang B. Y. Reinforcement of micro injection molded weld line strength with ultrasonic oscillation, Microsystem Technologies. DOI: 10.1007/s00542-009-0928-9

[86] Huang C. K., Chiu S. W., Formability and Accuracy of Micropolymer Compound with Added Nanomaterials in Microinjection Molding. Journal of Applied Polymer Science, Vol. 98, 1865–1874 (2005)

[87] Huang C.K., Filling and wear behaviors of micro-molded parts made with nanomaterials, European Polymer Journal 42 (2006) 2174–2184

[88] Zhang K. F., Lu Zhen, Analysis of morphology and performance of PP microstructures manufactured by micro injection molding, Microsyst Technol. (2008)14,(2):209-214

[89] Shimizu T, Murakoshi Y, Sano T et al (1998) Fabrication of micro–parts by high aspect ratio structuring and metal injection molding using the supercritical debinding methol. Microsyst Technol 5:90–92

[90] Yao D., Kimerling T. E., Kim B.. High-Frequency Proximity Heating for Injection Molding Applications. POLYMER ENGINEERING AND SCIENCE-2006 DOI 10.1002/pen.20548

[91] Nguyen-Chung T.. Flow analysis of the weld line formation during injection mold filling of thermoplastics, Rheol Acta ,2004,Vol.43: 240-245

[92] Diaranieh I.S., Haufe A., Wolf H. J., and Mennig G.. Computer simulation of weld lines in injection molded poly(methyl methacrylate), Polymer Engineering and Science, 1996, 15: 2050-2057

[93] Nguyen-Chung T., Plichta C., Mennig G.. Flow disturbance in polymer melt behind an obstacle, Rheol Acta,1998, Vol 37:299-305

[94] Piotter V., Mueller K., et al. Performance and simulation of thermoplastics micro injection molding, Microsystem Technoloyies,2002, No.8: P387-390

[95] Hung W.N.P., Ngothai Y., Yuan S., Lee C.W., and Ali M.Y.. Micromolding of three-dimensional components. The 10th International Conference on Precision Engineering Pacific Yokohama, Japan, July 18-20, 2001

[96] Lih S.T., Kharbas H.. Effect of process conditions on the weld-line strength and microstructure of microcellular injection molded parts, Polymer Engineering and Science, 2003, 1: 157-168

[97] Chang T. C., Faison E.. Optimization of Weld Line Quality in Injection Molding Using an Experimental Design Approach. Journal of Injection Molding Technology, 1999, 2:61-66.

[98] Koster R. P.. Importance of Injection Molding Parameters for Mechanical Performance of Cold Flow Weld Lines. Journal of Injection Molding Technology, 1999,3 :54-158.

[99] Kuehnert I., Mennig G. et al. Influence of Processing Conditions on the Weld Line in Doubly Injection-Molded Glassy Polycarbonate and Polystyrene: Micro indentation Hardness Study. Advances in Polymer Technology, 2005,1:14-20

[100] Lu C., Yu X.F., Guo S. Y.. Ultrasonic improvement of weld line strength of injection-molded polystyrene and polystyrene polyethylene blend parts. Polymer Engineering and Science,2005:1666-1672

[101] Cho K. et al. Evaluation of the weld-line strength of thermoplastics by compact tension test. Polymer Engineering and Science,1997,7: 1217-1225

[102] Kim J. K. et al. Morphology and mechanical properties of injection molded articles with weld lines, Polymer Engineering and Science, 1997,1: 228-241

[103] Mielwski D.F. et al. Weld line morphology of injection molded polypropylene, Polymer Engineering and Science, 1998,12:2020-2028

[104] Kim S.G., Sul N.P.. Performance prediction of weld line structure in amorphous polymer, Polymer Engineering and Science, 1986,Vol.26, 17.

[105] Tosello G., Gava A., Hansen H.N., Lucchetta G. and F Marinello., Characterization and analysis of weld lines on micro-injection moulded parts using atomic force microscopy (AFM), Wear, (2009)266, (5-6):534-538

[106] Tosello G. , Gava A. , Hansen H. N. and Lucchetta G. , Study of process parameters effect on the filling phase of micro-injection moulding using weld lines as flow markers, Int. J. Adv. Manuf. Technol. (2009) DOI: 10.1007/s00170-009-2100-1

[107] http://www.iap.tuwien.ac.at/www/atomic/instrumentation/afm

[108] Klug H.P. and Alexander L.E., X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials, 2nd ed., Wiley, New York (1974)

[109] Woo J.H., Polymer nanocomposites: processing, characterization and applications. McGraw- Hill, New York, (2006).

[110] Lozano K., Yang S.Y., Zeng Q., J. Appl. Poly. Sci., 93 (2004)1500

[111] Huang C.K., European Polymer Journal, 42(9), (2006) 2174

[112] Maris Knite, Igors Klemenok, Gita Shakale, Valdis Teteris, Janis Zicans, J. Alloys Compd.434-435(2007)850-853

[113] Zhang P., Zhang H. P., Li Z. H., Wu Y. P., Ree T. van, Polymers for Advanced Technologies, 20(6), (2009) 571

[114] Jou W. S., Cheng H. Z., Hsu C. F., J. Alloys Compd.434-435(2007)641-645

[115] Merz L., Rath S., Piotter V., Ruprecht R., Ritzhaupt-Kleiss J., Hausselt J.. Microsyst Technol, 8(2-3), (2002)129

[116] Gietzelt T., Piotter V., Jacobi O., Ruprecht R., Hausselt J.. Adv. Eng. Mater., 5(3), (2003)139

[117] Su B., Button T.W., Schneider A., Singleton L., Prewett P.. Microsyst. Technol., 8(4-5), (2002)359

[118] Huang C. K., Chiu S.W.. J. Appl. Poly. Sci., 98(5), (2005)1865

[119] Fellahi S., Meddad A., Fisa B., and Favis B.D., Advances in Polymer Technology, 14(3), (1995)165

[120] Bao P., Tjong S.C., Polym. Compos., 30, (2009)1749

[121] Jiang H. X., Ni Q. Q., Natsuki T., Polym. Compos., DOI 10.1002/ pc.20897 (2009)

[122] Lozano K., Barrera E.V., J. Appl. Poly. Sci., 79, (2001)125

[123] Fiske T., Gokturk H. S., Yazici F., and Kalyon D. M.. Effects of flow induced orientation of ferromagnetic particles on relative magnetic permeability of injection molded composites, Polymer Engineering and Science, 1997, 37, 5: 826

[124] Yamada K., Tomari K. et al. Fracture toughness evaluation of adjacent flow weld line in polystyrene by the SENB method. Polymer Engineering and Science, 2005:1059

[125] Grimm R.A., Welding processes for plastics. Adv. Mater. Process, Vol.147(1995)p27

[126] Kenney E., Designing plastic parts for ultrasonic assembly. Mach. Design, Vol. 21(1992)p65

[127] Pendleton J. W., U.S. Patent 3,298,065 (1965).

[128] Lemelson J., U.S. Patent 4,288,398 (1981).

[129] Sato A., Ito H., Koyama K.. Polym Eng Sci 2009, DOI 10.1002/pen

[130] Michaeli W., Spennemann A., Gärtner R., Microsyst Technol, Vol. 8(2002):55–57

[131] Bedenbecker M. , Bandorf R. , Bräuer G. , Lüthje H. and Gatzen H. H., (2008) Hard and soft magnetic materials for electromagnetic microactuators, Microsystem Technologies 14: 1949-1954

[132] Bandorf R. , Lüthje H. , Schiffmann K. , Beck M. , Gatzen H.-H. , Schmidt M. , Büttgenbach S. and Bräuer G., (2004)Submicron coatings for micro-tribological applications, Microsystem Technologies 10: 223-226

[133] Pichonat T., Gauthier-Manuel B., (2007)Recent developments in MEMS-based miniature fuel cells, Microsystem Technologies 13:1671-1678

[134] Quandt E., Holleck H., (1995)Materials development for thin film actuators, Microsystem Technologies 1(4): 178-184

[135] Rusu C., Jansen H., Gunn R., Witvrouw A.,(2004) Self-aligned 0-level sealing of MEMS devices by a two layer thin film reflow process, Microsystem Technologies 10: 364-371

Eidesstattliche Erklärung

Hiermit erkläre ich an Eides Statt, dass ich die bei der Fakultät für Material- und Naturwissenschaften der Technischen Universität Clausthal eingereichte Dissertation selbständig und ohne unerlaubte Hilfe verfasst und die benutzten Hilfsmittel vollständig angegeben habe.

Clausthal-Zellerfeld, den 16.04.2010

Lei Xie

Hiermit erkläre ich an Eides Statt, dass die eingereichte Dissertation weder in Teilen noch in Ihrer Gesamtheit einer anderen Hochschule zur Begutachtung vorliegt oder vorgelegen hat und dass ich bisher noch keinen Promotionsversuch unternommen habe.

Clausthal-Zellerfeld, den 16.04.2010

Lei Xie

Lebenslauf

Family Name, Given Name: Xie, Lei

Gender: Male

Date of Birth: July, 6th, 1980

Citizenship: P.R.China

Marital Status: married, with two kids (twins)

Education

Oct.2005 to Now	**PhD** in Material science and engineering Institute of Polymer Materials and Plastics Engineering , TU Clausthal, Clausthal-Zellerfeld, Germany
Sep. 2002 to Jun.2005	**Master** in Mechanical Manufacture and Automatic engineering (Honored) Central South University , Changsha, P.R.China
Sep. 1998 to Jun. 2002	**Bachelor** in Mechanical and electrical engineering (Honored) Central South University , Changsha, P.R.China

Profession

Since Oct. 2005	Scientific Coworker in Institute of Polymer Materials and Plastics Engineering, Clausthal University of Technology in Clausthal-Zellerfeld